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The Effect of Temperature on the Atomic Distribution in Liquid Potassium*

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X-ray diffraction patterns of liquid potassium at temperatures of 70°C, 200°C, 295°C and 395°C have been obtained, using Mo $K\alpha$ radiation. Three peaks appear in each pattern, and with increasing temperature, the peaks become somewhat less pronounced. The first, and most intense, peak appears at a scattering angle of 10° 36′ in the 70°C case, and it appears at 10° 16′ in the 395°C case. Fourier analysis applied to the above two cases gives the atomic distributions at these temperatures. In the 70°C distribution curve, the maximum of the first peak occurs at 4.64A, that of the second peak at 9.0A, and after this, the distribution rapidly becomes random. In the 395°C distribution curve, the maximum of the first peak occurs at 4.8A, that of the second at 9.2A, and beyond this the distribution becomes random more rapidly than in the 70°C case.

INTRODUCTION

THE so-called "structure" of a liquid can be given its most specific expression in the form of an atomic distribution curve. This curve represents the average distribution of atoms about a given atom. As a result of the theories of Zernike and Prins[1] and of Debye and Menke,[2] analysis of x-ray diffraction patterns of liquids leads to this atomic distribution curve. Determinations of this sort have been made for mercury,[2] for gallium[3] and for sodium[4] at two temperatures.[5] It is of interest to investigate various liquids at different temperatures for the information that may be obtained concerning the liquid state. In the present work, the effect of temperature upon the atomic distribution in liquid potassium has been investigated.

Previous work on the diffraction of x-rays by potassium has been done by Keesom[6] and by Randall and Rooksby.[7] They determined the position of the strongest peak in the pattern, and, making use of the Bragg equation for a crystalline solid,[8] they attempt to correlate the value of "d" so calculated with the spacing of the 110 plane in the crystal. The rough correlation and comparison of the results of the above two workers is given elsewhere.[9]

For quantitative determination of the atomic distribution, it is necessary to have as complete a diffraction pattern as possible. Knowing this to

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** On leave of absence from the Missouri School of Mines and Metallurgy, University of Missouri, Rolla, Mo.

[1] Zernike and Prins, Zeits. f. Physik **41**, 184 (1927).

[2] Debye and Menke, Erg. d. Tech. Rontgenkunde, II (1931).

[3] Menke, Physik. Zeits. **33**, 593 (1932).

[4] Tarasov and Warren, J. Chem. Phys. **4**, 236 (1937).

[5] Trimble and Gingrich, Phys. Rev. **53**, 278 (1938).

[6] Keesom, Amsterdam Akad. **30**, 341 (1927).

[7] Randall and Rooksby, Nature **130**, 473 (1932).

[8] Bragg, *The Crystalline State* (Macmillan Company, 1934), p. 15.

[9] Randall, *The Diffraction of X-rays and Electrons by Amorphous Solids, Liquids and Gases*, (John Wiley and Sons, 1934) p. 130.

angles of diffraction so large that interferences no longer play an appreciable part in the pattern, makes it possible to place the observed pattern in units of intensity per electron. Straightforward calculations then lead to the distribution of atoms about a given atom.

Experimental

Diffraction patterns of liquid potassium at 70°C, 200°C, 295°C and 395°C have been obtained, using Mo $K\alpha$ radiation reflected from a rocksalt crystal. The samples were contained in very thin-walled Pyrex capillary tubes, they were heated electrically, and their temperatures were determined by means of an iron Advance thermocouple with one junction close to the point where the x-rays passed through the sample. The capillaries were filled in a manner practically the same as was used in the case of sodium.[5] Because of the higher absorption of x-rays by potassium than by sodium, smaller diameter capillaries were used. This, however, required a reduction in the wall thickness of the capillaries in order to prevent excessive glass scattering. After several trials at 70°C, patterns were obtained with no perceptible rise in intensity at the point where the main peak of the glass pattern should appear. More difficulty was encountered in obtaining satisfactory patterns at the higher temperatures, especially at 395°C. In this case, thin-walled capillaries as used at 70°C were unable to stand the high temperature. It was finally necessary to use a pattern on which there appeared a small amount of excess scattering due to the main peak for glass. Correction for this glass scattering was necessarily approximate, but it was based on an experimentally determined pattern for the glass used in these experiments.

The capillary containing potassium was centralized in a cylindrical camera of 8.85 cm radius, and using new type Agfa film,[10] exposures of about 36 hours gave photographic densities high enough to measure with considerable certainty. The x-ray tube was operated at about 30 kv and 15 ma. Microphotometering the films, and converting to intensities in the usual manner resulted in the experimental intensity curves. The main peak in the 70°C case occurs at $\sin\theta/\lambda=0.130$, corresponding to a diffraction angle of 10° 36′ and that in the 395°C case occurs at $\sin\theta/\lambda=0.126$, corresponding to a diffraction angle of 10° 16′. These values are from curves corrected as mentioned below, but they are very little different from those taken from uncorrected curves. For intermediate temperatures, these quantities varied approximately linearly with the temperature. Further work was carried

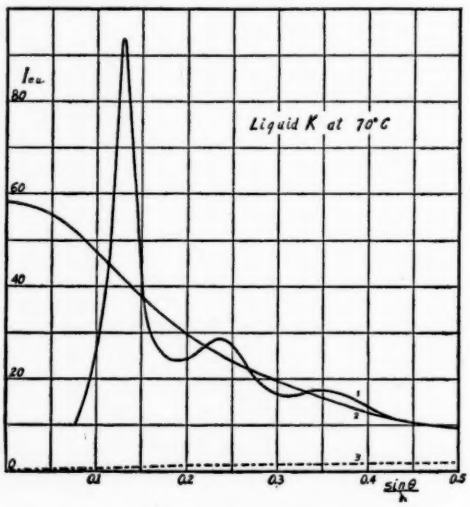

FIG. 1. Curve 1, corrected experimental intensity curve for liquid potassium at 70° C; curve 2, independent unmodified scattering; curve 3, incoherent scattering.

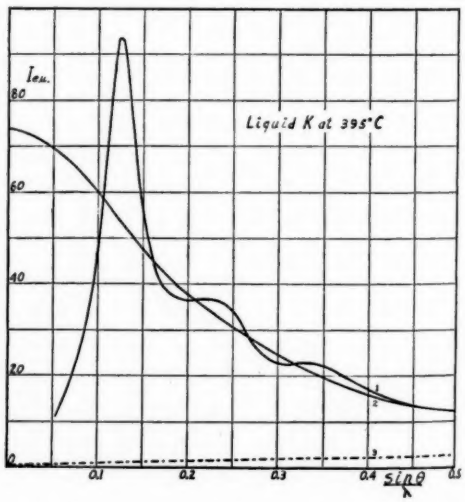

FIG. 2. Curve 1, corrected experimental intensity curve for liquid potassium at 395° C; curve 2, independent unmodified scattering; curve 3, incoherent scattering.

[10] Gamertsfelder and Gingrich, Rev. Sci. Inst. 9, 154 (1938).

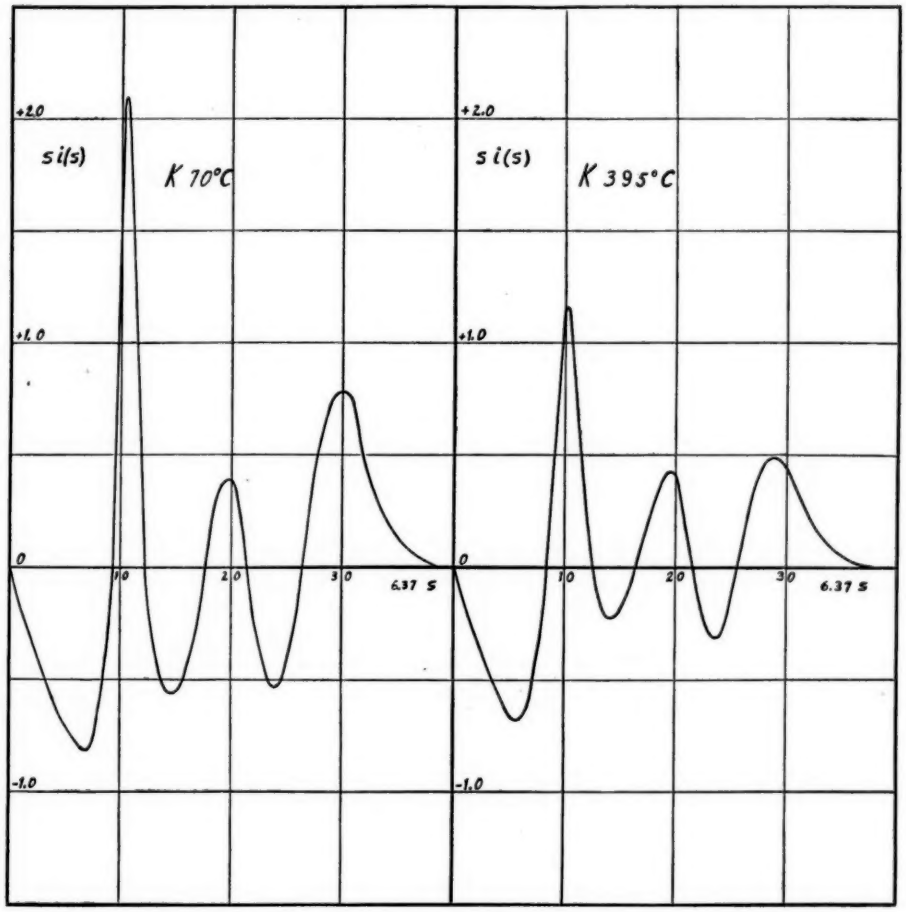

FIG. 3. Curves showing $si(s)$ functions for liquid potassium at 70°C and at 395°C.

out only for the two extreme temperatures, 70°C and 395°C.

APPLICATION OF THE FOURIER METHOD

The experimental intensity curves were corrected for absorption in the sample, for polarization both by crystal reflection and by diffraction from the sample, and for incoherent scattering from the sample. The absorption correction applied is that given by Blake.[11] The ratio of incoherent to total radiation was calculated from tables of "f" and "Σf^2".[12] The fully corrected intensity curve for the 70°C case is shown in Fig. 1, and that for the 395°C case is shown in Fig. 2. In both of these, 1 is the fully corrected intensity curve, 2 is the Nf^2, or coherent, curve, and 3 is the curve for the incoherent correction.

An outline of the theory may be found elsewhere,[13] but the equation used here is

$$4\pi r^2\rho(r)=4\pi r^2\rho_0+(2r/\pi)\int_0^\infty si(s)\sin rs\,ds, \quad (1)$$

where $4\pi r^2\rho(r)dr$ is the number of atoms between distances r and $r+dr$,

ρ_0 = average density of sample in atoms per unit volume,
$s=4\pi\sin\theta/\lambda$,
$i(s)=((I/N)-f^2)/f^2$,
I/N = unmodified intensity per atom in electron units,
f = atomic scattering factor.

[11] Blake, Rev. Mod. Phys. **5**, 169 (1933).
[12] Compton and Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand, 1935), p. 781.
[13] Warren and Gingrich, Phys. Rev. **46**, 368 (1934).

The quantity $si(s)$ is plotted against ks where k is a constant chosen for convenience in the use of the Coradi analyzer for evaluating the integral of Eq. (1). These curves are shown in Fig. 3 to illustrate the effect of temperature upon this function. Evaluation of the integral of Eq. (1) for various values of r leads to values of $4\pi r^2\rho(r)$ as a function of r.

Discussion of Results

The results of this analysis are shown in Fig. 4 for the 70°C case and in Fig. 5 for the 395°C case. The curve, $4\pi r^2\rho_0$ is shown in each case and it can be seen that the actual distribution approaches the average distribution more rapidly at the high temperature than at the low temperature. For 70°C, the maximum of the first peak occurs at 4.64A, and that for the second peak at about 9.0A. For 395°C, these maxima are shifted to 4.76A and 9.2A, respectively. If an arbitrary line is drawn along the large r slope of the first peak and extended to the axis in such a manner as to form a symmetrical, isolated curve, this curve covers an area of about 8 units in each case. This indicates that, on the average, there are roughly 8 atoms surrounding a given atom, but it is important to note that the distribution curves do not approach the axis between the first and second peaks. This indicates that there is a continual interchange of neighbors.

The effect of temperature can be shown very conveniently by plotting $\rho(r)$, the actual density, as a function of r. This is shown in Fig. 6. The horizontal line ρ_0 represents the average density at 70°C and the solid curve represents the actual density as a function of distance from a given atom at this temperature. At a distance of 15A from an atom, the actual density nearly equals the average density. The dotted curve for 395°C has its ordinates shifted so that it will oscillate about ρ_0 at 70°C. The maximum for the first peak for the 70°C curve occurs at 4.50A, and that for the 395°C curve occurs at 4.60A. It is to be noted that an increase in temperature causes all peak positions to be shifted to larger values of r, and that the high temperature curve is more highly damped.

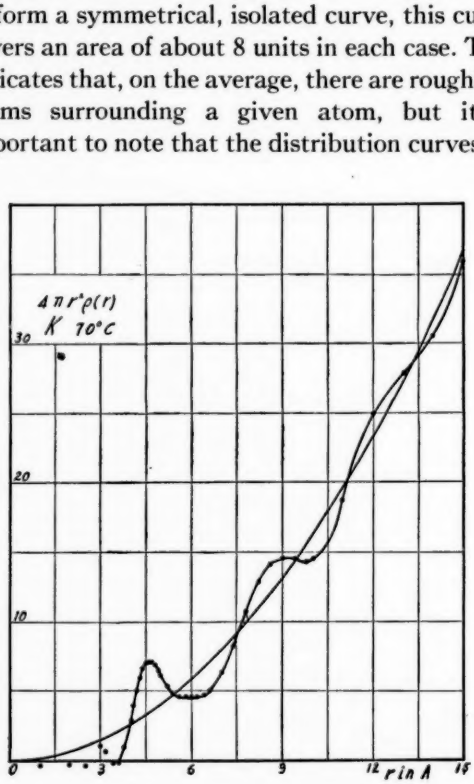

Fig. 4. The radial density distribution of atoms about any one atom in liquid potassium at 70° C.

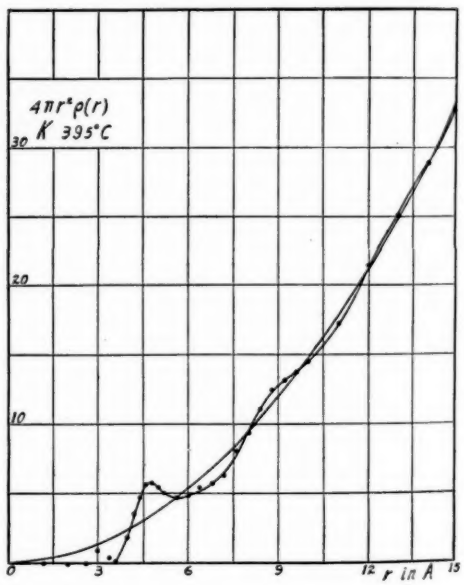

Fig. 5. The radial density distribution of atoms about any one atom in liquid potassium at 395° C.

As might be expected, these results are similar to those for sodium.[5] The peaks in the distribution curve occur at larger values of r in this case, due to the larger volume occupied by the potassium atom, but the general features of the curves for sodium and potassium are the same. The temperature effect in the two elements is

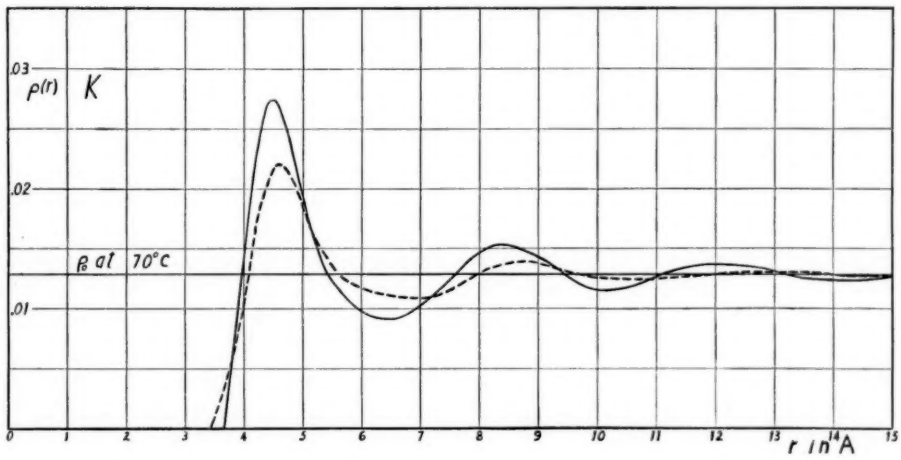

FIG. 6. The actual density in atoms per unit volume as a function of distance from any one atom in liquid potassium at 70°C. The dotted curve (with slightly shifted ordinate) shows that for liquid potassium at 395°C.

essentially the same. Although the distribution of atoms about a given atom retains a certain resemblance to that for the substance in the crystalline form for a few interatomic distances, the distribution rapidly becomes random beyond this region. An increase in temperature of the liquid reduces this resemblance, and it causes the random distribution to set in at smaller distances. That the general form of these curves can be explained on the basis of a mechanical model using steel balls has been pointed out by Debye and Menke.[2] An ingenious attempt to reconstruct the form of the density curve by experiment has been reported by Hildebrand.[14] It seems evident that the method here used to analyze diffraction patterns offers the most quantitative determination of the structure of a liquid, given by the atomic distribution function. These functions may also lead to the determination of interatomic forces in the liquid state.

It is a pleasure to acknowledge grants-in-aid-of-research made to one of us (N.S.G.) by the American Academy of Arts and Sciences from the Rumford Fund, and by the American Association for the Advancement of Science.

[14] Hildebrand, Science **80**, 125 (1934).

Primary Processes in Photodecomposition[1]

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When energy is absorbed by a molecule at a particular bond by a process of transition to a repulsive energy level or a sufficiently high point on an attractive level, rupture always results within one vibration period. All other photodecomposition processes are properly included under the title of predissociation. Thus, rupture may also result at the locus of absorption as the result of either spontaneous or induced adiabatic transition from an attractive to a repulsive or "weakly attractive" level. These are the only mechanisms of predissociation in diatomic molecules. In polyatomic molecules, spontaneous or induced shifts of energy or rearrangements of groups, resulting in decomposition, may also occur. Illustrations of the various processes suggested are cited from the photochemistry of sulfur, iodine, ozone, and the aldehydes. In the case of formaldehyde it has been possible to distinguish potential hypersurfaces and to indicate two different types of predissociation: one in a single hypersurface and the other a spontaneous transition between two hypersurfaces. The method used is extended to other aldehydes. Suggestions are made as to the interpretation of the photochemistry of several other substances and as to several problems which require solution.

THE term predissociation was introduced by Henri[2] to apply to diffuse regions of the ultraviolet absorption spectrum of certain substances distinctly different in appearance from the continuum or dissociation region. When, by the use of the Franck-Condon principle, predissociation spectra were explained[3] for diatomic molecules on the basis of an adiabatic transition from an attractive to a repulsive or "weakly attractive" state, it became customary to apply the term *predissociation* to the process which produced the system of diffuse absorption bands. More recently it has become necessary to speak of this process at length and in detail. In polyatomic molecules still a third use of the term predissociation has as a result sprung up; predissociation is said to occur as the last step in the involved series of perturbations through which the molecule goes as the result of the absorption of light.[4] As a result of this rather loose terminology the study of photodecomposition has acquired a complexity of interpretation and of statement which is neither desirable nor justified. It is proposed to simplify matters by confining the use of the term *predissociation* to the process itself, for it is with the mechanism of the process that the chemist is primarily concerned.

In Table I there is given a chart of the various types of processes which may occur on light absorption, the various types of reactions which may result and the appearance of the spectrum which may excite the particular process. For the purposes of illustration, three types of molecules have been used, namely, RX, $RA\begin{matrix}B\\C\end{matrix}$, and RABCD.

Excitation of a molecule, particularly if it be complicated, may result in any one of several

TABLE I. *Classification of photochemical decompositions.*

TYPE OF REACTION	TYPE OF PROCESS
1. Rupture into atoms or radicals	1. Rupture
a.	*a.* Energy absorbed at bond
i. $R-X+h\nu \rightarrow R+X$	i. Immediate rupture
ii*x*. $R-X \rightarrow R+X$	ii. Adiabatic transition
y. $R-X^*+M \rightarrow R+X+M$	*x*. spontaneous
	y. induced
b. $RA\begin{matrix}B^*\\C\end{matrix} \rightarrow R+BAC$	*b*. Energy transferred to bond
or	i. spontaneous
$RA\begin{matrix}B^*\\C\end{matrix} \rightarrow B+RAC$	ii. induced
2. Decomposition into groupings not occurring in original molecule	2. Rearrangement of molecule
$RA\begin{matrix}B^*\\C\end{matrix} \rightarrow RB+AC$	*a*. spontaneous
or	*b*. induced
$RABCD^* \rightarrow AB+RCD$	

[1] Paper presented before the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society, Dallas, Texas, Apr. 19, 1938.

[2] Henri, Comptes rendus **177**, 1037 (1923); Henri and Teves, Nature, **114**, 894 (1924); Comptes rendus **179**, 1156 (1924).

[3] Bonhoeffer and Farkas, Zeits. f. physik. Chemie **134**, 337 (1928); Kronig, Zeits. f. Physik **50**, 347 (1928).

[4] Cf. Sponer, *Molekülspektren*, Vol. 2 (Julius Springer, Berlin, 1935), p. 237.

excited states. Corresponding to any one such excited state, there is a certain probability that decomposition will occur within one vibration period after its creation. We will define a simple rupture process as one in which, on the average, decomposition occurs at the locus of absorption in less than one vibration period after the creation of the excited state.[5a] All other decomposition processes are included under the title of predissociation.[5b] Referring to Table I, it may be seen that this is the case for every process except 1*ai*. The literature is replete with discussions as to whether or not predissociation or "simple decomposition" occurs in various cases. Our point is that with a precise definition of terms a decision is readily reached in most cases. Thus for example in the ketones, although the energy is absorbed in the C=O bond, there is never any indication of rupture of that bond. During the lifetime of the activated state (which may be extremely short), some shift of energy or position within the molecule occurs so that rupture actually takes place at some other bond (e.g., a C−C bond) or bonds as the result of absorption at a C=O bond.

However, the mere fact that dissociation takes place at the locus of absorption is not in itself an indication that it is not a predissociation process. When the excited state is such that as a part of the normal vibration the molecule separates into two halves the process may be called immediate rupture. When transition to a second excited state precedes such rupture, a predissociation process is involved.

Sulfur

An unambiguous illustration of these concepts is found in the case of sulfur. The energy relationships in the normal and excited S_2 molecule are illustrated qualitatively in Fig. 1 according

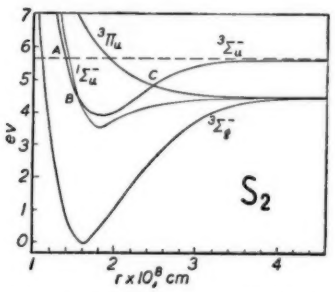

FIG. 1. Potential energy diagram for S_2

to the designations of Lochte-Holtgreven.[6] Excitation to the $3\Sigma_u^-$ level above the point *A* results in immediate rupture (1*ai*)

$$S_2 \rightarrow S(^3P) + S(^1D). \quad (1)$$

On the other hand, when excitation occurs to a point on the $3\Sigma_u^-$ level below *A* and above *C* there exist two possibilities of transition to other potential curves. At *C* there is a probability of transition to the repulsive $^3\Pi_u$ state. Once transition to that state occurs, dissociation immediately follows.

$$S_2(^3\Sigma_u^-) \rightarrow S_2(^3\Pi_u), \quad (2)$$

$$S_2(^3\Pi_u) \rightarrow 2S(^3P). \quad (3)$$

Such decomposition is a predissociation process (1*aiix*) and is produced by absorption in the region 2615–2435A. The spectrum is quite blurred even at very low pressures (0.1 mm);[7] from its fuzziness we may estimate that the lifetime of the S_2 molecule after absorption of energy is less than 10^{-11} sec. In this case, since the reaction 2 occurs very readily, it seems that the selection rules permit the transition. However, the conditions in the neighborhood of point *B* are different. At low pressures the absorption spectrum 2799–2615A is quite sharp indicating that there is a forbidden transition,[8] e.g.

$$S_2(^3\Sigma_u^-) \rightarrow S_2(^1\Sigma_u^-). \quad (4)$$

[5a] Incidentally, it should be emphasized that this definition is subject to considerable modification for polyatomic molecules. The meaning of *vibration period* is somewhat vague in the case of a molecule executing Lissajous figures.

[5b] The case of an adiabatic transition between two energy levels not resulting in decomposition, which was suggested by Franck, Sponer and Teller (reference 16) to account for the diffuseness of the SO_2 bands at wave-lengths greater than those corresponding to the heat of dissociation, is excluded from this definition.

[6] Lochte-Holtgreven, Zeits. f. Physik **103**, 395 (1936). The figure we use is different from his in that we favor the value of 4.45 ev for the dissociation energy of the normal state.

[7] Rosen, Zeits. f. Physik **52**, 16 (1928).

[8] There has been some discussion as to whether the second state is $^1\Sigma_u^-$ or $^3\Pi_g$ (cf. the case of Te_2, Kondratjew, Zeits. f. Physik **92**, 741 (1934)). However, the designation is immaterial to this argument. Our interest lies in the fact that the transition at *B*, in contrast with *C*, does not occur spontaneously.

The selection rules responsible may be weakened by strong fields such as are produced, for example, by neighboring molecules. Thus it is found that increase of the S_2 vapor pressure causes the absorption region 2799–2615A to become blurred. It appears that the transition at B is more properly written

$$S_2(^3\Sigma_u^-)+M \rightarrow S_2(^1\Sigma_u^-)+M, \quad (5)$$

where M may represent an external field. The subsequent reaction is

$$S_2(^1\Sigma_u^-) \rightarrow 2S(^3P). \quad (6)$$

The process involved is an induced predissociation and is of the type 1*aiiy*.

Tellurium

The conclusions on S_2 receive additional support from the observations of Kondratjew and Lauris[9] on Te_2. Here also there is induced predissociation (1*aiiy*) lying to the long wavelength side of spontaneous predissociation (1*aiix*). In this case, however, it is suggested that the crossing of states at the point B, such as shown in Fig. 1, does not actually occur. Instead Kondratjew and Lauris indicated the $^3\Sigma_u^-$ and $^3\Pi_g$ levels (cf reference 8) as running close together at that point. It is interesting that in this case Olsson[10] induced predissociation by the effect of an intense electromagnetic field.

Iodine

The energy relationships of the various states of the iodine molecule are illustrated qualitatively in Fig. 2 as given by Mulliken.[11] Excitation of the molecule to a point in the $^3\Pi_{0u}^+$ state above A (2.47 ev) leads to immediate rupture (1*ai*) corresponding to the beginning of the continuum at 4990A. The low pressure (0.1 mm) iodine absorption spectrum is otherwise discrete. The iodine atoms produced in the continuum can be detected by their absorption spectrum. Relatively few are produced on illumination in the discrete region. Whether these few result from molecules starting in a higher vibrational level of the ground state or from iodine induced transitions from the $^3\Pi_{0u}^+$ state to one of the other $^3\Pi_u$ states shown cannot be definitely stated. However, it is known that, when a magnetic field is applied[12] or the pressure is increased or inert gas added,[13] the yield of iodine atoms in the discrete region of the I_2 absorption spectrum is greatly increased. The result is evidently attributable to induced predissociation (1*aiiy*). Kondratjew and Polak[14] studied the effect of added gases on the absorption coefficient of I_2 in the discrete region of the spectrum. They found three maxima in the effect which, according to them, correspond to the three vibrational quantum numbers $v'=22$, 29, and 39. Presumably, we may infer that these three regions of increased absorption correspond respectively to three disallowed transitions from the $^3\Pi_{0u}^+$ state to the other $^3\Pi_u$ states shown in Fig. 2.

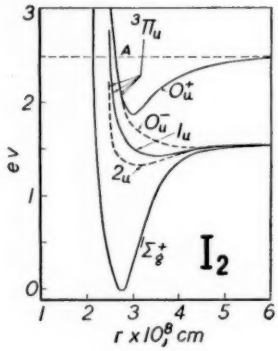

FIG. 2. Potential energy diagram for I_2.

The Significance of the Threshold of Induced Predissociation

We have seen in the case of S_2 (Fig. 1) that there is a close correspondence between the threshold of induced predissociation and the heat of dissociation into normal atoms. On the other hand, in the case of I_2 (Fig. 2) there is no such correspondence. The agreement in the case of S_2 is fortuitous and depends on the fact that there are energy levels existent in such a position

[9] Kondratjew and Lauris, Zeits. f. Physik **92**, 741 (1934).
[10] Olsson, Comptes rendus **204**, 1182 (1937).
[11] Mulliken, Phys. Rev. **36**, 1440 (1930); Rev. Mod. Phys. **4**, 1 (1932).
[12] Turner, Zeits. f. Physik, **65**, 464 (1930).
[13] Turner, Phys. Rev. **41**, 627 (1932).
[14] Kondratjew and Polak, Physik. Zeits. Sowjetunion **4**, 764 (1933).

as not to require excess energy for the decomposition. The mere existence of such energy levels is, of course, not enough; transitions to these energy levels are first necessary. We see that in S_2 the transition resulting in decomposition at an energy input corresponding to the bond strength is forbidden. The transition required must be induced by an external field. In I_2, although the transitions to other energy states may likewise be induced, the initial excited state is so high that an amount of energy in excess of the heat of dissociation is required. Three factors are necessary for the threshold of predissociation to correspond to the bond strength: (1) Absorption of light must actually occur at frequencies corresponding to the heat of dissociation. This requires that there is an upper state to which transition is permitted at such an energy difference from the lowest state. (2) There must be a possibility of an adiabatic transition to another energy state (neglecting selection rules) at a potential energy level corresponding to the heat of dissociation. (3) If the latter transition is forbidden, there must be an external field to induce it. Obviously, the greater the number of energy states in which the molecule may exist, the closer the correspondence between the threshold of induced predissociation and the bond strength.[15]

Ozone

For the polyatomic molecules the processes immediately become more complicated. We cannot draw a potential energy diagram for the excited molecule although we can speak in a vague way of the properties of the hypersurfaces corresponding to the different energy levels. Thus, the intersection of the hypersurfaces may be likened to the intersection of lines in the diatomic case.[16] Decomposition may, of course, result immediately from the absorption act by transition from the normal state to a repulsive or "weakly attractive" hypersurface. This may occur in the case of simple triatomic molecules. Thus

$$O_3+h\nu\rightarrow O_2+O.$$

The principal evidence in this case is the existence of the continuum. That a predissociation process also occurs is indicated by the presence of diffuse bands superimposed on the continuum. These bands indicate the existence of an excited state with a mean life long enough to give some degree of definition but still short compared to the time between collisions. Below 2700A the spectrum appears to be entirely continuous. Predissociation is theoretically possible in ozone for all wave-lengths less than 11,500A. For the diffuseness to extend throughout the visible and near ultraviolet, as has been reported, it is virtually certain that transfers, from the excited state produced by light absorption, must occur to more than one level. The possibility exists that some of these transfers are not spontaneous, but are induced by the fields of the other molecules present (cf. the case of S_2). The observations on the absorption spectrum of O_3 have always been made with considerable pressures of both O_2 and O_3. Both of these molecules are paramagnetic and therefore would be expected to be particularly efficient in causing predissociation. It would be of interest to have observations made on pure ozone at low pressures to see if the spectrum will become discrete as was found by Lochte-Holtgreven for S_2.

Formaldehyde

The evidence clearly indicates that the absorption of energy in aldehydes and ketones takes place in the C=O bond. Nevertheless, as has already been mentioned, rupture never occurs at that point. According to the definition we are using, predissociation is involved. The precise type of predissociation may be judged from a resumé of the evidence. In the case of formaldehyde, a fine line absorption spectrum[17]

[15] If the excitation occurs from a high initial vibrational state it is actually possible for the threshold of induced predissociation to correspond to an energy less than the heat of dissociation from the lowest vibrational state.

[16] Cf. Franck, Sponer and Teller, Zeits. f. physik. Chemie **B18**, 88 (1932).

[17] The absorption spectrum of formaldehyde has been discussed by (*a*) Henri and Schou, Zeits. f. Physik **49**, 774 (1929); (*b*) Henri, *The Structure of Molecules*, P. Debye, editor (Blackie and Son, Ltd., London, 1932), p. 126; (*c*) Herzberg, Trans. Faraday Soc. **27**, 378 (1931); (*d*) Dieke and Kistiakowsky, Proc. Nat. Acad. Sci. **18**, 346 (1932); Phys. Rev. **45**, 4 (1934); (*e*) Price, J. Chem. Phys. **3**, 256 (1935). The fluorescence has been discussed by (*f*), Herzberg and Franz, Zeits. f. Physik **76**, 720 (1932); (*g*) S. Gradstein, Zeits. f. physik. Chemie **B22**, 384 (1933).

extends through the region 3570–2750A. A diffuse region extends from 2750 to ~2500A; a continuous background begins at <2670A and extends to lower wave-lengths. The products formed by the photolysis are almost entirely H_2 and CO. The products may be formed either in a single primary act after activation or by an intermediate process involving the production of atomic hydrogen and free formyl radicals. We have not found any mention in the literature of an experiment seeking to establish the production of H atoms by a direct test (e.g., the para-orthohydrogen conversion method or the guard-mirror method). However, there is indirect evidence in some experiments performed in the presence of oxygen[18] that although free H atoms are formed below 2700A none are produced by photolysis in the discrete region of the spectrum. The wave-length 2750A, at which point the diffuse spectrum begins, corresponds to ~103 kcal. per mole, which is of the order of, or slightly higher than, the strength of the C−H bond.[19]

We have already discussed the possibility of correspondence between the threshold of induced predissociation and the strength of the bond ruptured. The point was emphasized that the greater the number of possible states in which a molecule may exist the closer such correspondence. For polyatomic molecules there are not only a great number of possible states (hypersurfaces in our potential diagram) into which induced transitions can occur (factor 2) but there is also greater irregularity in the form of the hypersurfaces involved, thus increasing the probability of light absorption at a frequency corresponding to the strength of the ruptured bond (factor 1). Consequently, we may reasonably infer that the minimum amount of absorbed energy required to effect rupture in a polyatomic molecule, in the absence of restrictions due to selection rules, probably corresponds fairly closely to the strength of the ruptured bond.

In the case of formaldehyde the close correspondence between the beginning of the diffuse spectrum and the strength of the C−H bond, particularly in view of the evidence for production of atomic hydrogen, indicates that nearly all the energy absorbed in the C=O bond becomes available for rupture of a C−H bond within a period less than 10^{-11} sec. Processes 1*bi* or 1*bii* are clearly involved. The diffuseness of the spectrum is not always a sufficient clue for deciding between a spontaneous and an induced process, particularly when as in a polyatomic molecule the various rotational levels may lie so closely together as to overlap. In this case, the fact that the diffuseness so closely corresponds to the beginning of the production of atomic hydrogen suggests that it is caused by the same process which produces the atomic hydrogen, i.e. by a spontaneous predissociation process involving a transfer from a long-lived activated state to a repulsive or weakly attractive state (see the case of sulfur) from which rupture results (1*bi*). Ordinarily, we might say that to decide unambiguously between an induced and a spontaneous predissociation process in a polyatomic molecule it would be necessary to have information concerning the effect of added gases or increased pressure on the quantum yield of the reaction concerned (i.e., the production of atomic hydrogen below 2750A). However, in this case the spectral evidence is so clear that we may predict that such an investigation would show no effect because the spontaneous process (1*bi*)

$$HCHO^* \rightarrow H + HCO \qquad (1)$$

occurs in a time which is short as compared with the interval between collisions.

Fluorescence of excited formaldehyde has been observed at 3530, 3400 and 3270A indicating that the life period of molecules excited in that portion of the discrete region is $\sim 10^{-8}$ to 10^{-7} sec. Norrish and Kirkbride[20] have suggested that the decomposition in this region is due to an induced predissociation process (2*b* according to our classification)

$$HCHO + M \rightarrow H_2 + CO + M, \qquad (2)$$

where M may be another formaldehyde molecule.[21] The basis for the statement that it may

[18] Patat, Zeits. f. physik. Chemie **B25**, 208 (1934); Löcker and Patat, ibid. **B27**, 431 (1934).

[19] Cf. Trenner, Morikawa and Taylor, J. Chem. Phys. **5**, 203 (1937); Kistiakowsky, J. Phys. Chem. **41**, 175 (1937).

[20] Norrish and Kirkbride, J. Chem. Soc. 1518 (1932).

[21] To be sure the reaction $HCHO + HCHO \rightarrow 2H_2 + 2CO$ is also acceptable on energetic grounds; however we neglect

be induced predissociation is the sharp structure of the spectrum; spontaneous processes usually cause a diffuse structure. In order definitely to establish which process is involved (2*b* or 2*a*) experiments on the effect of pressure or of added gas are necessary. Herzberg and Franz[17f] state that addition of air up to 100 mm pressure does not diminish the fluorescence appreciably. This indicates that a collision of the second kind mechanism with nitrogen or oxygen does not dissipate the energy of the excited molecule and that neither nitrogen nor oxygen (the latter of which should be particularly effective) induces predissociation. Thus, we may infer that at 3530–3270A at any rate, the predissociation process is spontaneous, rather than induced as suggested by Norrish and Kirkbride. At those wave-lengths we must view the mechanism as an excitation to a stable hypersurface in which the molecule may remain for some time executing a complicated Lissajous figure.[16] After a period of 10^{-9} sec. decomposition occurs in the same hypersurface. The sharp line spectrum indicates that if a transition between hypersurfaces be the process it is restricted by selection rules. The effect of pressure is always to weaken the restriction imposed by selection rules and to lessen the life of the excited state. Since such an effect is not observed[17f] we must conclude that such a transition does not occur in this case and that the reaction actually is

$$HCHO^* \rightarrow H_2 + CO. \qquad (3)$$

The Mechanism of Predissociation by Rearrangement

As just indicated there are two possible mechanisms for decomposition by rearrangement. A molecule may undergo a transition from an excited state to another hypersurface. In the second hypersurface it executes a Lissajous figure one configuration of which is the same as that of a collision between the molecules resulting from the decomposition. From that configuration, decomposition may occur just as if it were merely the separating half of the collision of the two molecules. If the predissociation process be spontaneous according to our definition (type 2*a*) we could change the model in one respect. The molecule could be thought of as remaining in the same excited hypersurface until decomposition occurs. The distinction between these two processes is *not* academic. It is real and the two can actually be distinguished as seen for formaldehyde in the range 3530–3270A.

The introduction of these concepts gives us further insight into the mechanism of the predissociation of formaldehyde below 2750A. The nature of the products (atomic hydrogen and free formyl) indicates that a different hypersurface is involved in this case. The fact that the diffuseness appears in a sudden blurring of the spectrum without change in vibration structure indicates that the absorption process involves an excitation to the same hypersurface on both sides of 2750A. Consequently, we must conclude that the diffuseness below 2750 is due to an adiabatic transition to a second repulsive or "weakly attractive" hypersurface. The fuzziness at the low pressures involved (~35 mm[17a]) indicates that the transition is spontaneous.

Other Aldehydes

The discrete absorption spectrum of acetaldehyde extends from 3484 to 3050A[22] at which wave-length the diffuse spectrum begins. A continuum underlies the whole spectrum. The main distinction between formaldehyde and acetaldehyde lies in the fact that there is a weaker bond, the C–C bond, to be broken in the latter. 3050A corresponds to ~93 kcal. per mole which is of the order of, or slightly higher than, the strength of the C–C bond.[19] On the other hand, there is indirect evidence for slight free radical production[23a] at wave-lengths of 3130A and less. This is in agreement with what would be expected from the conclusions of Franck and Herzfeld[23b] that in complicated molecules, where 12 or more available (i.e., vibrational) degrees of freedom can contribute

its consideration because according to the principle of microscopic reversibility such a reaction would appear extremely unlikely.

[22] Schou, J. chim. phys. **27**, 27 (1929); Leighton, Chem. Rev. **17**, 393 (1935).

[23a] Blacet and Roof, J. Am. Chem. Soc. **58**, 278 (1936). Cf. Rollefson, J. Phys. Chem. **41**, 259 (1937); Burton, ibid. **41**, 322 (1937).

[23b] Franck and Herzfeld, J. Phys. Chem. **41**, 97 (1937).

energy, a photochemical reaction can proceed with an apparent energy deficiency of ~7 kcal. On the basis of this reasoning we should expect the threshold of free radical production would shift slightly toward shorter wave-lengths with increase in complexity of the aldehyde molecule.[24] For the more complex aldehydes it has not been possible to resolve the rotational structure. The spectra appear diffuse in the range 3400–2700A and show a continuous background extending to 2350A. Nevertheless, we feel justified in assuming on the basis of the analogy to formaldehyde that two types of predissociation are involved, namely processes 1*bi* and 2*a*. The former accounts for the production of free radicals from 3050A down toward shorter wave-lengths

$$RCHO \rightarrow R + HCO; \qquad (1)$$

the latter

$$RCHO \rightarrow RH + CO \qquad (2)$$

produces ultimate molecules in the primary act throughout the whole absorption range by a spontaneous predissociation. In the cases of acetaldehyde[25a] and propionaldehyde[25b] there is actually a slight decrease of quantum yield with pressure at 3130A. Although the evidence is not conclusive, the slight decrease which was observed in these cases is compatible with the assumption of the spontaneous predissociation process.

In the case of *n*-butyraldehyde[24] the evidence indicates that approximately 75 percent of the molecules decomposed at 3130A yield C_3H_8 and CO in the primary act. The quantum yield (of CO molecules produced) actually increases with pressure at 3130A. Thus it appears that in *n*-C_3H_7CHO, as in the other aldehydes, the decomposition into radicals is the spontaneous predissociation process represented by reaction 1, but that, unlike the other aldehydes, *n*-C_3H_7CHO decomposes into stable molecules via an induced predissociation process (2*b*)

$$RCHO + M \rightarrow RH + CO + M. \qquad (3)$$

The result suggests that the large size of the unit involved (i.e. C_3H_7) increases the complexity of the pattern of oscillation through which the molecule must pass prior to a decomposition into ultimate molecules. The time required for decomposition in the original excited state is thus increased and the intrusion of an outside field (e.g., of another molecule) promotes transfer to another excited hypersurface in which the arrangement is suitable for a rapid division into C_3H_8 and CO.

There is also in the case of *n*-C_3H_7CHO a new decomposition reaction characteristic of higher aldehydes and ketones, namely

$$CH_3CH_2CH_2CHO + M \rightarrow CH_3CHO + C_2H_4 + M. \qquad (4)$$

This reaction is written as an induced predissociation process because it takes place even less readily than reaction 3 at 3130A. Since reaction 3 is induced, reaction 4 *cannot* be spontaneous. Of two reactions, one spontaneous and the other induced, the spontaneous reaction takes place the more readily.

We see that for *n*-butyraldehyde, excitation transfers the molecule to an attractive energy state *a* (cf. S_2 below the point *B*). On excitation by sufficiently short wave-lengths transfer to a repulsive energy state *b* occurs spontaneously and the molecule decomposes into free radicals by reaction 1 (cf. the transition at *B* in S_2. At all wave-lengths in the absorption region considered, we may imagine a condition such as suggested for Te_2, except that in this case the induced transition can take place to either of two "repulsive" hypersurfaces, one *c* yielding reaction 3, the other *d* yielding reaction 4.

Other Cases

It should be noted that we have not presented an example of process 1*b*ii. It is possible that careful study of the photolysis of acetone in the continuum[26] or of azomethane[27] may yield an example of such a case.

[24] Leighton, Levanas, Blacet and Rowe, J. Am. Chem. Soc. **59**, 1843 (1937), claim that their results with *n*-butyraldehyde at 3130A can be explained by the assumption of 15 percent decomposition via a free radical mechanism. Here also the evidence is indirect.

[25a] Leighton and Blacet, J. Am. Chem. Soc. **55**, 1766 (1933).

[25b] Leighton and Blacet, J. Am. Chem. Soc. **54**, 3165 (1932).

[26] (*a*) Cf. Spence and Wild, J. Chem. Soc. 352 (1937); (*b*) Norrish, Crone and Saltmarsh, ibid. 1456 (1934); (*c*) Damon and Daniels, J. Am. Chem. Soc. **55**, 2363 (1933).

[27] See, for example, the effects of foreign gases, Goldfinger, Compt. rendus **202**, 1502 (1936). Also Davis, Jahn and Burton, J. Am. Chem. Soc. **60**, 10 (1938).

The alkyl iodides probably are a case of rupture occurring in the bond at which absorption takes place. There is no evidence of structure in the near ultraviolet absorption regions. The strength of the C−I bond is ~44 kcal.[28] The continua begin at ~3500A.[29] If the rupture which occurs at the C−I bond were a predissociation process (1*bi* or ii) we might, according to the principles already expressed, expect a closer correspondence (since these are polyatomic molecules) between the bond strength and the threshold of the continuum. We conclude therefore that the process involved is immediate rupture at the locus of absorption (1*a*). The fact that no fluorescence is reported in the continua of these compounds is compatible with such a conclusion.

This list of a few compounds is by no means exhaustive. We have neglected mention of the complex ketones, the aliphatic acids, nitrites and many other substances which would prove of interest. The few that have been mentioned are just sufficient to illustrate the various mechanisms we have suggested.

Some Remarks on Spectra

When energy is absorbed at a bond and rupture follows within one vibration period the absorption spectrum is continuous. The converse is by no means always true. The continuum of acetone begins at ~3000A and no discrete structure is observable below 2495A.[26a] Nevertheless, fluorescence is detected down to 2537A indicating that the excited states produced in this apparent continuum have a life considerably in excess of one vibration period. In polyatomic molecules, where the rotation levels lie close together, the apparent absence of a structure is no indication of the existence of a "true" continuum. Such factors as fluorescence, effect of pressure on quantum yield, and the nature of the products must be taken into consideration. Thus, in such cases as the aldehydes, ketones, aliphatic acids, etc., we may disregard the possibility not only of process 1*ai*, which is associated with the "true" continuum, but also of processes 1*aiix* and *y*. The aliphatic acids are particularly interesting because although the absorption is apparently continuous[30] predissociation, according to our definition, is the only process that can occur. The experimental evidence is sufficient only to indicate that it is of both the two types 1*b* (i or ii) and 2 (*a* or *b*).[31]

We have seen in the case of iodine that discrete absorption is associated with induced predissociation (1*aiiy*). On the other hand, a similar spectrum in the case of formaldehyde was shown to be related to a spontaneous process (1*bi*). In the case of the higher aldehydes both a spontaneous (2*a*) and an induced (2*b*) process are associated with the diffuse absorption spectrum. Clearly, the characteristics of the absorption spectrum alone are no assurance of the type of process occurring. It is proposed that to simplify matters the term predissociation be reserved for the processes themselves and that we continue to describe spectra in terms of their naive characteristics: i.e. as discrete, diffuse and continuous, those terms being as we observe them and not as we imagine they ought to be.

[28] Kohlrausch, *Der Smekal-Raman-Effeckt* (Julius Springer, Berlin, 1931).
[29] Cf. Sen-Gupta, Bull. Acad. Sci., U.P. **2**, 115 (1933).
[30] Ley and Arends, Zeits. f. physik. Chemie **B17**, 177 (1932).
[31] Cf. Burton, J. Am. Chem. Soc., **58**, 1645, 1655 (1936); Henkin and Burton, ibid. **60**, 831 (1938). See however, Terenin, Acta Physiocochim. U. S. S. R., **3**, 181 (1935) for work in the extreme ultraviolet.

The Raman Spectrum of Boron Trifluoride Gas

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The Raman spectrum of BF_3 was photographed using a purified preparation obtained from the thermal decomposition of $C_6H_5N_2BF_4$. Of the lines observed, that with the frequency 888 cm^{-1} is certainly, and the band at 439–513 cm^{-1} is probably due to BF_3. The Raman frequencies and the infra-red results of Bailey *et al.* are assigned to the fundamental modes of vibrations.

IN a former paper by Anderson, Lassettre and Yost[1] on the Raman spectra of the boron halides, the assignment arrived at for boron trifluoride was stated to be a tentative one. This was due to the fact that, in spite of efforts to avoid it, the boron trifluoride was contaminated with silicon tetrafluoride (and possibly small amounts of other impurities, e.g., SO_2) as was shown by the presence of at least one Raman line of silicon tetrafluoride in the photographs. The infra-red spectrum of BF_3 has been determined by Professor Bailey *et al.*,[2] and the results were not in complete agreement with those of the Raman spectrum, the most important difference being the lines assigned to the isotopic doublet ν_3. In order to resolve, if possible, these difficulties and discrepancies, the experiments on the Raman spectrum were repeated and with special attention given to the preparation of pure material.

The BF_3 was prepared by the thermal decomposition of benzene diazonium fluoborate ($C_6H_5N_2BF_4$).[3] This compound was prepared from purified materials, and at the stages where hydrofluoric acid was involved, platinum dishes or paraffin coated beakers were used to avoid contamination with SiF_4. Since strong sulfuric acid is not present during the formation of BF_3 (gas) there is little likelihood that SO_2 is present. It is to be emphasized that fluorides formed in reactions requiring concentrated sulfuric acid contain small quantities, 0.1 percent or less, of SO_2. The volatile compounds, C_6H_5F, BF_3, N_2, resulting from the decomposition of the diazonium salt were passed through two traps cooled with solid CO_2, and one cooled to $-100°$ ($CHCl_3$, 31 percent $+C_2HCl_3$, 69 percent cooled to freezing point with liquid air) before being condensed with liquid air. The first three traps served to remove C_6H_5F, and the BF_3 was collected in the liquid-air trap. After pumping off the N_2, the BF_3 was allowed to vaporize into an evacuated storage flask. Apiezon grease was used on all stopcocks and was found to be slightly attacked by the BF_3, but any volatile product formed was small and was, for the most part, frozen out in the $-100°$ trap. An amount of BF_3 sufficient to give a final pressure of 75 pounds gauge was condensed in a quartz Raman tube which was then sealed off. A water-cooled mercury arc, operated with a current of 150 volts and 8 amperes, and burning in quartz was used as a source of 2537A radiation.

When first exposed to the arc the contents of the tube clouded up slightly in a few minutes. On standing, the cloud or precipitate settled, and further illumination did not result in the formation of any more of it. The amount of precipitate was so small that it could hardly be seen on the tube walls. The exposures, with Eastman 50 plates, varied from 28 to 73 hours. Comparison spectra of the mercury arc were taken at the end of each exposure before turning off the arc. Enlargements of the plates were made on process film, and contact prints were made of the latter on extreme contrast Velox paper. Such prints are very convenient for examining a spectrum for faint or diffuse lines. The iron arc comparison spectrum was photographed on both sides of each Raman spectrum.

The results are presented in Table I. The

[1] Anderson, Lassettre and Yost, J. Chem. Phys. **4**, 703 (1936).
[2] Bailey, Hale and Thompson, J. Chem. Phys. **5**, 275 (1937); Proc. Roy. Soc. **161**, 107 (1937).
[3] Balz and Schiemann, Ber. **60**, 1186 (1927). These authors describe the compound $C_6H_5N_2BF_4$; Mr. Henri Lévy of this laboratory is the first to suggest and use the method described above for preparing pure BF_3.

numbers in parenthesis adjoining the frequency values are estimated intensities. The assignments refer to the nomenclature and diagrams given in the former paper, by Anderson, Lassettre and Yost.

The lines 1037 and 1100 cm^{-1} found by Anderson, Lassettre and Yost and assigned to the isotopic doublet, ν_3, were found here in the spectrum of the Hg arc. These lines did not appear in the comparison spectrum of Anderson, Lassettre and Yost but were plainly present in the Raman spectrum; it appears from this and other results that the relative intensity of an Hg line in the scattered spectrum may be greater than in a direct exposure of the arc. The explanation may lie in the sensitizing effects arising from continuous fluorescence present in the scattered spectrum. The 1395 cm^{-1} line assigned to 2 ν_2 by Anderson, Lassettre and Yost was not found; two faint Hg lines at 1376 and 1405 cm^{-1} were found and may be responsible for the previous result.

The only line that is certainly present in the Raman spectrum of BF_3 is the strong one at 888 cm^{-1}. The band at 439–513 cm^{-1} is probably due to BF_3, since it appears in experiments that differ both in technique and method of preparation of the compound.

TABLE I. *The Raman spectrum of* BF_3 (*g*).

FREQUENCY IN cm^{-1}		REMARKS
888	(10)	ν_1
439 to 513	(2)	Band corresponds to band at 415 to 465 found by A.L.Y. and assigned to ν_4. Barely possible that it is due to quartz.
769 to 854	(1)	Band may correspond to 783 of A.L.Y., and explained as resonance between ν_1 and $2\nu_4$.
723	(0)	Presence in Hg arc doubtful.
745	(0)	
1126	(0)	Possibly in Hg arc though not plainly.
1143	(0)	
1448	(0)	Might be in Hg arc. Bailey found 1448 and 1501 in infra-red and assigned them to isotopic doublet, ν_3.
1481	(00)	

TABLE II.

FREQUENCY IN cm^{-1}	ASSIGNMENT
888	$\nu_1(1)$, Symmetrical or swelling vibration. *R*. Fobidden in *IR*.
722	$\nu_2(1)$, *B* atom moves to plane of *F* atoms. *IR*. Forbidden in *R*.
694	
1448	$\nu_3(2)$, Isotopic doublet, *IR*; not certain in *R*.
1501	
439 to 513	$\nu_4(2)$, Broad band in *R*.

The final assignment of the frequencies obtained from the Raman spectrum and infra-red to the fundamental modes of vibration can now be made with moderate assurance that it is correct. The scheme shown in Table II is in complete agreement with that arrived at by Bailey, Hale and Thompson.[2] Their bands at 1448 and 1501 cm^{-1} are resolved and it seems correct to consider them as an isotopic doublet. They have chosen to resolve analytically the rather broad band at 722 cm^{-1} into two and then ascribe the two to a second isotopic doublet. This seems a questionable procedure in general, but in this case the result is possibly correct. The numbers in parentheses give the degeneracies; *IR* and *R* refer to the infra-red and Raman spectrum, respectively. The BF_3 molecule is known to have the F atoms at the corner of an equilateral triangle with the B atom in the center and in the same plane.[4]

[4] H. Lévy and L. O. Brockway, J. Am. Chem. Soc., **59**, 2085 (1937).

Raman Spectra of Hydrogen and Deuterium Sulfides in the Gas, Liquid and Solid States

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Raman spectra have been obtained for H_2S and D_2S as gas, liquid and solid. Only one frequency has been obtained in the gas and liquid although three are permitted by the selection principles. In the solids, a single line and a close doublet have been obtained. With the available infra-red and Raman data, it is not possible to make quantitative calculations of isotope effect, force constants, angle or anharmonic factors.

1. INTRODUCTION

THE hydrogen sulfide molecule is known to belong to the symmetry group, C_2v and therefore three vibrational frequencies should be observed, both in the infra-red and in the Raman spectrum. Following the conventional nomenclature of Dennison,[1] we call ν_1 the symmetrical valence vibration, ν_2 the deformation vibration and ν_3 the antisymmetrical valence vibration. Previous work by Bhagavantam[2] resulted in but one frequency, 2615 cm^{-1}, in the Raman spectrum of H_2S gas and one frequency, 2578 cm^{-1} in the liquid. Sirkar and Gupta[3] reported four frequencies in solid H_2S at 80, 2523, 2547 and 2558 cm^{-1}. The only work on the Raman spectrum of D_2S is that of Dadieu and Kopper[4] who reported a single line of 1875 cm^{-1}. This frequency is certainly for the liquid since they also obtained 2578 cm^{-1} for H_2S. They report 1880 and 2585 cm^{-1} for HDS but this is obviously incorrect since these are the frequencies for H_2S and D_2S.

The older work on the infra-red absorption of H_2S is erroneous due to the presence of impurities. Recent work on vibration-rotation bands has been done with instruments of low dispersion by Bailey, Thompson and Hale,[5] under higher dispersion by Nielsen[6] and collaborators and in the photographic infra-red by Cross[8] and by Carvin. Similar experiments have been made on D_2S and HDS by Bailey, Thompson and Hale[5] and by Nielsen and Nielsen.[8]

The purpose of the present work was to re-examine the Raman spectra of both H_2S and D_2S in all three states in the hope of obtaining better values for the three fundamental frequencies.

2. EXPERIMENTAL

The H_2S was drawn from a tank obtained from the Matheson Company, and was reported to be 99.7 percent pure. It was dried over P_2O_5 and frozen in liquid air. After several fractional distillations, the H_2S was distilled into the Raman tube at a pressure of about 2 atmospheres. The tube was made of Pyrex and was similar to that described by Teal and MacWood[9] except that the platinum diaphragm used by them was omitted. The tube was 86 cm long and 3 cm in diameter. It was completely surrounded by a helical Pyrex arc containing neon and mercury as described by Glockler and Davis.[10] The potential on the arc was approxi-

[1] In the descriptive system of Mecke, these are called $\nu(\pi)$, $\delta(\pi)$ and $\nu(\sigma)$, respectively.
[2] S. Bhagavantam, Nature **126**, 502 (1930).
[3] S. C. Sirkar and J. Gupta, Ind. J. Phys. **10**, 227 (1936).
[4] A. Dadieu and H. Kopper, Nature **136**, 235 (1935); Akad. Anz. **11**, 13 (1935). These are authors' abstracts of a paper presented before the Vienna Academy; the paper does not appear to have been published. The results are also quoted in *Tables Annuelles de Constantes et Données Numériques, No. 1. Deutérium et Composés de Deutérium.* G. Champètier. (Hermann et Cie., Paris 1937). A. Dadieu and W. Engler, ibid., have reported Raman frequencies for H_2Se, D_2Se and HDSe. The results for the latter appear to refer also to a mixture.
[5] C. R. Bailey, J. W. Thompson and J. B. Hale, J. Chem. Phys. **4**, 625 (1936).
[6] H. H. Nielsen and E. F. Barker, Phys. Rev. **37**, 727 (1931); H. H. Nielsen and A. D. Sprague, ibid. **37**, 1183 (1931); A. D. Sprague and H. H. Nielsen, J. Chem. Phys. **5**, 85 (1937).
[7] P. C. Cross, Phys. Rev. **47**, 7 (1935); J. Chem. Phys. **5**, 370 (1937); F. D. Carvin, ibid. **5**, 159 (1937).
[8] A. H. Nielsen and H. H. Nielsen, J. Chem. Phys. **5**, 277 (1937).
[9] G. K. Teal and G. E. MacWood, J. Chem. Phys. **3**, 760 (1935).
[10] G. Glockler and H. M. Davis, J. Chem. Phys. **2**, 881 (1934).

mately 3000 volts and the current through it was about 350 milliamperes. A Schmidt and Haensch Universal spectrograph was used with 2 Rutherford prisms. The dispersion in the region of the Raman lines was about 16.5A per mm. A lens of 7 cm focal length was used to focus the scattered radiation on the slit and to insure that no light scattered by the walls should enter the spectrograph. With a slit width of 0.1 mm, satisfactory exposures of the gas could be obtained in about 100 hours, although the Raman line could be seen on the plates after an hour or two. Eastman spectroscopic plates, type I-J were used and standard Fe lines were used for a comparison spectrum. The plates were measured on a comparator giving readings reproducible to ± 0.001 mm.

For observations on the liquid and the solid, smaller Raman tubes were used which were supported in an unsilvered Dewar flask. The latter was surrounded with a helical arc of similar design to that described above. The Raman tubes were cooled with dry ice alcohol for the liquid and liquid air for the solid. Satisfactory exposures were obtained for the liquid and solid in about 4 hours.

D_2S was prepared from pure aluminum sulfide and 99.6 percent D_2O with subsequent distillation as in the preparation of H_2S.

3. Experimental Results

The experimental results are shown in Table I. The frequencies given in Table I are average values as determined from two or more plates. In some cases, scattering was observed from both the 4358A and 4047A mercury line. Agreement between two or more plates in each case was better than ± 2 cm^{-1}. The Raman line in the gas and in the liquid is quite sharp. In the solid, the close doublet is rather diffuse and about half as intense as the single line. The latter is quite sharp. In the experiments on the solids, we also observed a Raman line of liquid oxygen, the frequency of which was in good agreement with the experiments of McLennan and McLeod.[11]

[11] J. C. McLennan and J. C. McLeod, Nature, **123**, 160 (1929).

Table I. *Observed Raman frequencies (cm^{-1} in vacuum) of H_2S and D_2S (gas, liquid and solid).*

	Gas	Liquid	Solid
H_2S	2610.8	2573.6	2520.8
	——	——	2545.8
	——	——	2553.7
D_2S	1891.6	1866.3	1832.5
	——	——	1848.5
	——	——	1853.4

4. Discussion

The gas

The single frequency obtained in the gas is undoubtedly ν_1. The fact that the other two frequencies do not appear is probably a matter of intensity. It is not possible at present to make any calculations on the relative intensities of Raman lines since very little is known regarding the change of polarizability with displacement. A qualitative explanation of the appearance of only one frequency may be given however. If the molecule were linear and hence belonged to the symmetry group, $D_{\infty h}$, ν_1 would be the only frequency active in the Raman effect. As the angle becomes less than 180°, this frequency will probably still remain more intense in the Raman effect than the other two frequencies which were inactive in the linear molecule. This fundamental vibration has not been observed in the infra-red for either H_2S or H_2O. Van Vleck and Cross[12] have offered the following explanation for the inactivity of ν_1 in the infra-red spectrum of H_2O. As the hydrogen atoms approach the oxygen atom, the molecules become more ionic in character and the accompanying migration of charge averages out in such a way that there is no appreciable change in the electric moment. The same argument applies to H_2S and also shows that in this mode of vibration there will be a maximum change in the polarizability and hence the line should appear in the Raman effect with considerable intensity. Although the resolving power of our spectrograph was sufficiently great to separate ν_1 from ν_3 and ν_2, no trace of them could be seen on plates given exposures over 400 times as

[12] J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).

long as that needed to photograph ν_1. It can thus be said that ν_1 appears in the Raman effect with an intensity of more than 400 times that of ν_2 or ν_3.

Although ν_1 does not appear in the infra-red as a fundamental, it is active in combination bands in both H_2O and H_2S. In the former case, both ν_1 and ν_2 as observed in the Raman effect[13] have frequencies about 50 cm^{-1} greater than the corresponding calculated results obtained from infra-red spectra.[14] A similar discrepancy appears to exist in D_2O also.[15] No satisfactory explanation has yet been given for this shift but it has been assumed that the behavior is shown only by H_2O and D_2O. While there seems to be no reason why the Raman and infra-red frequencies should be different, we should like to point out that there is no definite experimental proof that H_2O is a unique case. In H_2O, H_2S and HCN,[16] the fundamental frequency has been observed only in the Raman effect. In other cases, such as NH_3 and SO_2, the infra-red frequencies have been observed but complete rotational analyses have not been made and there is some doubt about the origin of the bands. In other cases, the Raman effect has only been obtained on the liquid. It is not possible to say whether there is a difference between the infra-red and Raman spectra in H_2S and D_2S from the present experimental data. Since ν_1 has not been observed in the infra-red it is necessary to calculate its frequency from the position of overtone and combination bands and this can only be done if the anharmonic factors in the vibrational energy are known. Nine observed frequencies are required to calculate these factors and there are not nine bands for H_2S known with certainty since the frequencies as determined by different investigators are not in complete agreement. Conclusions have been drawn concerning the presence or absence of a collected Q branch from the general appearance of the rotational structure or of the band envelope and while the appearance will probably be similar to the charts of Dennison,[17] transitions involving J values greater than 4 and intensity changes may alter the appearance considerably. We therefore believe that calculations of anharmonic factors, angle and force constants of H_2S and of D_2S based on the present data are of doubtful value unless a complete rotational analysis can be made such as that of the band at 9911 cm^{-1} by Cross.[7]

The liquid

The shift of the Raman frequency accompanying a change of state from gas to liquid has been discussed by Buchheim[18] and his considerations may be extended to the shift from liquid to solid. The changes in the spectrum due to association in solution have been discussed by Wolkenstein[19] and these results may also be extended to liquids and solids. The experimentally observed shift, $\Delta\nu = \nu(\text{gas}) - \nu(\text{liquid})$ is 37.2 cm^{-1} or 1.4 percent for H_2S and 25.3 cm^{-1} or 1.3 percent for D_2S. The shift is towards lower frequencies which is observed in most polar compounds. However, in some cases, as for example, liquid ethane,[20] the shift is in the opposite direction for two of the vibrational frequencies. For nonpolar compounds, the shift is usually less than 0.5 percent.

The solid

Our experimental results[21] on H_2S are in good agreement with earlier work of Sirkar and Gupta.[3] They, however, have observed a frequency of 80 cm^{-1} both as a Stokes and anti-Stokes line. We have not attempted a measurement in this region since the experimental difficulties attending the recognition and correct assignment of a frequency so near the exciting line introduce considerable uncertainty[22] concerning the meaning of such lines of low frequency.

The close doublet is probably to be associated with ν_1, although one should expect it to be more intense than the other line. Taking the center of gravity of the doublet, the ratio of gas

[13] H. L. Johnston and M. K. Walker, Phys. Rev. **39**, 535 (1932); D. F. Bender, ibid. **47**, 252 (1935).
[14] L. G. Bonner, Phys. Rev. **46**, 458 (1934).
[15] G. W. King, J. Chem. Phys. **5**, 405 (1937).
[16] K. N. Choi and E. F. Barker, Phys. Rev. **42**, 777 (1932).
[17] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).
[18] W. Buchheim, Physik. Zeits. **36**, 694 (1935).
[19] M. Wolkenstein, Acta Physicochim. **4**, 357 (1936).
[20] G. Glockler and M. M. Renfrew, J. Chem. Phys. **6**, 295 (1938).
[21] In a preliminary communication, G. M. Murphy and J. E. Vance, J. Chem. Phys. **5**, 667 (1937), we reported only two lines in the solid. These results were obtained with somewhat smaller dispersion than that used here.
[22] See, for example, I. R. Rao and P. Koteswaram, Phil. Mag. **25**, 90 (1938).

frequency to solid frequency is 0.98 for both H_2S and D_2S. A splitting of this type has been observed in other solids[23] and is usually attributed to the effect of electric fields in the crystal lattice.

The single remaining frequency cannot be associated with ν_2 since this deformation frequency is usually much lower than the other two. Taking the gas frequencies for H_2S and D_2S from the work of Nielsen[6,8] as 2685 and 2000 cm^{-1} for ν_3, $\Delta\nu = 164$ cm^{-1} or 6.1 percent for H_2S and 167.5 cm^{-1} or 8.4 percent for D_2S. The ratio of gas to solid frequency is 0.74, for both H_2S and D_2S.

From x-ray data, Vegard[24] has concluded that H_2S is linear in the solid state. This conclusion conflicts with the fact that ν_1 and ν_3 appear in the Raman spectrum of the solid. Further, this interpretation of the data has been disputed by Sirkar and Gupta[25] who concluded from their own Raman data and the x-ray results of Vegard that the molecule is bent, the angle being about 108°. However, their arguments are based upon erroneous conclusions of Dadieu and Kohlrausch[26] who obtained an angle of 90° from the spectroscopic data. While the angle is not known definitely, it is almost certainly not 90°. Both Dadieu-Kohlrausch and Sirkar-Gupta have used a simplified valence-force potential energy curve for the molecule. As shown above and in many other places, this sort of potential energy function may not be used except as a rough approximation for actual molecules. Moreover, the angle is very sensitive to slight changes in the frequency and for the latter, the actual mechanical frequency corrected for anharmonic terms must be used and not the observed frequency. All questions regarding angle, force constants and isotope effect can only be settled with more and better experimental data.

[23] A. A. Sidorova, Acta Physicochim. **7**, 193 (1937).
[24] L. Vegard, Nature **126**, 916 (1930).
[25] S. C. Sirkar and J. Gupta, Ind. J. Phys. **11**, 119 (1937).
[26] A. Dadieu and K. W. F. Kohlrausch, Physik. Zeits. **38**, 165 (1932).

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Fractionation of the Lithium and Potassium Isotopes by Chemical Exchange with Zeolites*

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A study has been made of the fractionation of the lithium isotopes by electrolysis and of the lithium, potassium, and nitrogen isotopes by chemical exchange with zeolites. The fractionation factor obtained by a "batch" electrolysis of lithium chloride solution was 1.039. The normal abundance ratio of the lithium and potassium isotopes was determined and found to be 11.71 ± 0.14 for $Li^7 : Li^6$ and 14.10 ± 0.09 for $K^{39} : K^{41}$. The fractionation factor for the lithium isotopes in exchange with sodium zeolite was found to be 1.022. A partial separation of the lithium, potassium and nitrogen isotopes has been affected using long columns filled with zeolites. Both an increase and a decrease of about 25 percent from the normal abundance ratio has been obtained for the lithium isotopes and a change of about 10 percent for the potassium and nitrogen isotopes. Some of the factors involved in the mechanism of the process are discussed.

INTRODUCTION

RECOURSE may be had to a number of different methods in attempts to separate the isotopes of an element. One may choose a method more or less directly dependent on physical properties related to the masses of the isotopes such as diffusion, distillation, or deflection in an electric and magnetic field using large capacity mass spectrographs. Electrolysis or reaction velocity may also lead to some fraction

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ation. Chemical exchange methods[1] have been used with success by Urey and his co-workers for the fractionation of a number of isotopes as, for example, oxygen,[2] carbon,[3] nitrogen,[4, 5] and more recently sulfur,[6] lithium and potassium.

The use of large capacity mass spectographs has led to the separation of only minute quantities of the lithium[7] and potassium[8] isotopes. Lewis and Macdonald[9] have obtained a marked increase in the concentration of Li^6 by countercurrent extraction of a lithium amalgam with an ethyl alcohol solution of lithium chloride. They estimated a lower limit of 1.025 for the fractionation factor of the process.

Encouraged by the successful separation of the hydrogen isotopes by electrolysis, a number of investigators started work on the separation of the lithium isotopes using a flowing mercury cathode. Of these may be cited the work of Eucken and Bratzler[10] on lithium sulphate; Taylor and Urey[11] on lithium hydroxide; and Holleck[12] and Hutchison[13] on lithium chloride. The fractionation factors obtained were respectively 1.07 (upper limit), 1.02, 1.07 and 1.062.

Heavesy and Logstrup[14] have used a non-equilibrium distillation method and achieved some fractionation of the potassium isotopes. Nier and Hustruled[15] also obtained a small fractionation by a similar method during some studies on the radioactivity of potassium. Brewer[16] has found that small changes in the isotope ratio occur in certain natural processes.

Some further experiments on the fractionation factor for the electrolysis of the lithium isotopes have been made by the present authors. A 38 percent lithium chloride solution was electrolyzed in the same cell with the same current density as that used in the electrolysis of lithium hydroxide except that a graphite anode was used and the average temperature was 36°C. The mercury was stirred rapidly and the gases evolved at the anode stirred the solution. After electrolysis of 450 g of lithium chloride to 5 g, the ratio of the isotopes in the solution remaining in the cell was changed to 13.8 which gives a fractionation factor of 1.039. The lower fractionation factor may arise either from the higher current efficiency resulting from stirring the mercury or an effect due to dilution. The other investigators have electrolyzed in several stages taking the first part of the lithium electrolyzed for the next stage such that they were always electrolyzing from a concentrated solution. In the "batch" method as we have used there is a continual decrease in concentration.

In the course of the experiments on the electrolysis of lithium hydroxide, a sample was found in which the ratio of Li^7 to Li^6 was 12.5 instead of the normal ratio 11.6. It appeared that somewhere in the manufacture appreciable fractionation had occurred. Upon tracing the original source of the material, the manufacturer was hesitant in giving any information regarding its manufacture. One of the most general methods used to obtain lithium is to heat the silicate base ore, such as lepidolite, with potassium sulphate.[17] A zeolite type reaction takes place in which potassium is exchanged for lithium. Such replacement may be preferential with respect to one of the isotopes. This led to an investigation of the possibility of fractionation of the isotopes of the alkali elements by the so-called base exchange reactions with zeolites. A preliminary report was made by Taylor and Urey[11] in which small changes in the ratio of the lithium and the nitrogen isotopes from ammonium ion were described. Further experiments were made on potassium isotopes and reported by Taylor, Brewer and Urey.[18] The results have also been

[1] Urey and Greif, J. Am. Chem. Soc. **57**, 321 (1935).
[2] Huffman and Urey, J. Ind. Eng. Chem. **29**, 531 (1937).
[3] Urey, Aten and Keston, J. Chem. Phys. **4**, 622 (1936).
[4] Urey and Aten, Phys. Rev. **50**, 575 (1936).
[5] Urey, Huffman, Thode and Fox, J. Chem. Phys. **5**, 856 (1937).
[6] Thode, Gorham and Urey, J. Chem. Phys. **6**, 296 (1938).
[7] Rumbaugh and Hofstad, Phys. Rev. **50**, 681 (1936).
[8] Smythe and Hemmendinger, Phys. Rev. **51**, 128 (1937).
[9] Lewis and Macdonald, J. Am. Chem. Soc. **58**, 2519 (1936).
[10] Eucken and Bratzler, Zeits. f. physik. Chemie **174**, 269 (1935).
[11] Taylor and Urey, J. Chem. Phys. **5**, 597 (1937).
[12] Holleck, Zeits. f. Elektrochem. **44**, 111 (1938). See also Zeits. f. angew. Chemie **49**, 33 (1936).
[13] Hutchison, Dissertation. Ohio State University (1938).
[14] Heavesy and Logstrup, Zeits. f. anorg. allgem. Chemie **161**, 1 (1928).
[15] Nier and Hustruled. Private communication.
[16] Brewer, J. Am. Chem. Soc. **58**, 365 (1936); ibid. **59**, 869 (1937).
[17] Osborg, *Lithium* (The Electrochemical Society, New York City, 1935).
[18] Taylor, Brewer and Urey, Rochester Meeting Am. Chem. Soc.

confirmed by Brewer and Reed[19] in their laboratory using "greensand." A more complete discussion of the process and the results obtained on lithium and potassium will follow.

Mass Spectrometer for Analysis of Isotopic Abundance Ratios

One of the most difficult problems in studies on the separation of isotopes is the analysis of the results. One may make direct determinations on a mass spectrometer or make determinations of the atomic weight, density, or other properties associated with the mass of the atoms. During the first part of the investigation, methods of analysis were tried which depended upon a difference in the density of compounds containing the isotopic atoms in different ratios. One was an isopiestic density method and another the flotation of lithium fluoride crystals in an organic liquid mixture by variation of temperature and pressure. Both were comparative methods and required a long time for purification so a mass spectrometer of the Dempster type, as modified by Bainbridge[20] and Brewer[16] was built to analyze the samples.

The apparatus was constructed and operated in most respects as described by Brewer.[16] The positive ions produced by heating a platinum disk previously impregnated with the sample were drawn through the slit by applying 270 volts for potassium and 810 volts for lithium. The resolving chamber had a radius of 5 cm and was evacuated to a pressure of 1 to 5×10^{-6} mm Hg. The positive ion current was carried to a DuBridge[21] balanced circuit amplifying system and the amplified current was read from the galvanometer scale. In making a determination the accelerating voltage was held constant and the magnetic field was varied until the galvanometer deflection was a maximum. This current was taken as a measure of the abundance of the isotope. The magnetic field was then changed until another isotope was brought to the collecting plate. If the amplification was linear, the ratio of the galvanometer deflections could be taken as the ratio of the abundances of the isotopes. However, this was not always the case and the potentiometric method described by Cohn and Urey[22] was used to get the exact ratios.

The principal source of error in the determinations was in reading the height of the smaller peak which is from one-tenth to one-fifteenth the larger one (25 to 40 cm). If the zero point drifts owing to unsteadiness of the amplifier, or if the positive ion beam is not constant, as is often the case, then there are further errors involved in reading the deflections. In general the readings are probably not better than 0.3 to 0.4 mm which means a possible error of 2 to 2.5 percent in a single determination. Averages for different filaments of the same material sometimes varied as much as 2 to 3 percent, especially if solid material remained on the disk or a gas was given off during heating. Also if the pressure was not kept sufficiently low the resulting poor resolution decreased the accuracy. However, there was generally no background between the lithium peaks and seldom as much as 0.1 to 0.2 mm between the potassium peaks. In general, it is considered that the ratios reported are not better than ±0.1 to ±0.2 from the true ratio, that is, about 1.5 to 2 percent.

Determinations of the normal ratio of the lithium isotopes made by different investigators[12] show wide variations. While our purpose was not the accurate determination of the abundance ratio, it is of interest to report our results in confirmation of the accepted values. The average value of the ratio $Li^7 : Li^6$ taken from determinations made at different times during the research is 11.71 ± 0.14 which is in fair agreement with those of Bainbridge[20] and Brewer,[23] 11.51 ± 0.31 and 11.60 ± 0.06, respectively. Using 6.940 for the atomic weight of lithium and Bainbridge's[24] values for the masses of the atoms (6.0145 ± 0.0003 and 7.0145 ± 0.0007), a value of 11.84 is obtained calculated on the basis of Aston's[25] new value for He (4.00391). This is in good agreement with the mass-spectrographic measurements.

Potassium is known to have three isotopes with mass numbers 39, 40 and 41. The ratio of K^{39} to

[19] Brewer and Reed, Nitrogen Fixation Laboratory. Private communication.
[20] Bainbridge, J. Frank. Inst. **212**, 3176 (1931).
[21] DuBridge and Brown, Rev. Sci. Inst. **4**, 532 (1933).
[22] Cohn and Urey, J. Am. Chem. Soc. **60**, 679 (1938).
[23] Brewer, Phys. Rev. **47**, 571 (1935).
[24] Bainbridge, Phys. Rev. **46**, 56 (1933).
[25] Aston, Nature **137**, 357 (1936).

K^{41} is given by Nier[26] as 13.96 ± 0.1 and Brewer[27] as 14.25 ± 0.03. Manley[28] using the ratio of the heights of the peaks in nuclear magnetic moment studies obtains the value 13.4 ± 0.5. The isotope of mass 40 is radioactive and is present to the extent of only one part in 8000.[29] The ratio of K^{9} to K^{41} obtained from the average of a number of determinations made during this research is 14.10 ± 0.09 which is in good agreement with the above values.

The Nature of Zeolitic Substances

Many substances, particularly those which tend to form negative ionic micelles in the sense used by McBain,[30] possess the property commonly referred to as base exchange. That is, they exchange a positive ion held by the substance for one in solution. The most widely studied and well-known of these substances are the complex hydrated alumino-silicates known as zeolites. A review of the voluminous literature on these substances is given by Randall and Cann,[31] Wiegner[32] and Jenny.[33] Many naturally occurring zeolites such as the glauconites (greensands), the ultramarines, sodalite, nephilite, and the clays such as bentonite, all show a greater or less tendency to exchange their bases depending on their composition and structure. Artificial zeolites have been made by many different methods as, for example, the reaction of a solution of sodium aluminate and sodium silicate in such proportions that the product has an approximate composition represented by the empirical formula $Na_2O\cdot Al_2O_3\cdot 6SiO_2\cdot xH_2O$. The sodium is replaceable by other positive ions, a divalent ion replacing two monovalent ones.

It has been known for a long time that the alkali and alkaline earth elements exhibit specific ion effects and may be arranged in a lyotrope or Hofmeister series according to their effectiveness in replacing one another from the zeolite. For an artificial zeolite, the ions of the alkali and alkaline earth elements give the following series:

$$Mg^{++}<Li^{+}<Ca^{++}<Na^{+}<Ba^{++}<NH_4^{+}<K^{+}<Rb^{+}<Cs^{+}<H^{+}.$$

That is, lithium is the least strongly held while cesium is the most strongly held of the alkali elements. The order of the alkali elements is that of the decreasing size of the hydrated ion.[33] A change in the conditions affecting the solvation of the ions such as a change in the nature of the solvent[32] or temperature[34] will change the behavior of the ions. Such change in behavior with change of conditions may prove important in the fractionation of isotopes.

If one shakes a quantity of zeolite with a solution of another positive ion, equilibrium is established in ten to twenty minutes and partial replacement takes place according to the reaction

$$A^{+}+BZ\leftrightarrows B^{+}+AZ.$$

Addition of more ion A^{+} replaces more B^{+} approximately in conformity to the mass law up to a certain maximum, beyond which only a small increase in exchange will take place with increased addition of A^{+}. The amount of exchange is essentially independent of dilution[35] but depends principally on the ratio of the total quantities of the two electrolytes and zeolites present. Concentrations may be used only when reference is made to a fixed total volume. Specific properties of the zeolites and ions make it impossible to give equations applicable to all systems. Of the many proposed, one of the most generally applicable equations used to express the amount of base exchange at equilibrium is one of the type given by Rothmund and Kornfeld:[36]

$$K=\frac{AZ}{BZ}\cdot\left[\frac{(B^{+})}{(A^{+})}\right]^{\beta}, \qquad (1)$$

where K is an equilibrium constant, (A^{+}) and (B^{+}) are the concentrations of the two ions in the given volume of solution, and AZ and BZ are the equivalents of the two forms of zeolites present. The constant β varies from 0.5 to 1.0 for different

[26] Nier, Phys. Rev. **48**, 283 (1935).
[27] Brewer, Phys. Rev. **48**, 640 (1935).
[28] Manley, Phys. Rev. **48**, 921 (1936).
[29] Nier, Phys. Rev. **48**, 283 (1935). Brewer, Phys. Rev. **48**, 640 (1935).
[30] McBain, Trans. Faraday Soc. **9**, 99 (1913); Kolloid Zeits. **40**, 1 (1926).
[31] Randall and Cann, Chem. Rev. **7**, 369 (1930).
[32] Wiegner, J. Soc. Chem. Ind. **50**, 65T (1931).
[33] Jenny, J. Phys. Chem. **36**, 2217 (1931).
[34] Jaeger, Trans. Faraday Soc. **25**, 320 (1939).
[35] Wiegner and Muller, Zeits. Pflanz Dung. **14A**, 321 (1929).
[36] Rothmund and Kornfeld, Zeits. f. anorg. allgem. Chemie **103**, 129 (1918).

systems and expresses the fact that the ratio of the two forms of zeolite are not necessarily the same as the ratio of the ions in solution.

According to the scheme used by Austerweil[37] the zeolite is considered to be a solid solvent nonmiscible with the solution of the cation which exchanges. The laws of extraction should apply and there should be a distribution of the two cations depending on the "solubility" or concentration ratio of the two zeolites. To extract a total fraction E of a cation from solution there would be required n extractions as given by $(1-\alpha')^n=1-E$ where α' is the exchange or distribution coefficient.

Starting with the properties and behavior of zeolites as outlined above and the assumption that one isotope is taken up more readily than the other, a method must be devised to multiply the single stage effect many times. Any of the batch or batch-counter current methods of extraction[38] may be followed. A continuous counter current method as used in the separation of the nitrogen isotopes[5] by exchange of NH_3 and NH_4^+ would be more effective but the difficulties of counter current motion are much greater for a solid and liquid than for a liquid and gas. The use of a long column packed with zeolite seems to be the most favorable scheme. A number of different procedures may be followed. A solution of lithium may be passed through a column containing a sodium zeolite. All the way down the column one isotope should be held back more than the other and the first lithium coming through should have a changed isotope ratio. This first sample will be called the "leading sample." After the column is converted to a lithium zeolite a solution of sodium chloride may be passed through the column. One isotope is replaced more readily than the other by the sodium and the last lithium coming through the column should have the isotope ratio changed in the opposite direction to that of the leading sample. This last sample will be called the "tailing sample."

Another procedure is one similar to that used in the separation of closely related organic substances by the recently developed methods of chromatographic analysis.[39, 40] According to this method a tube is filled with a suitable absorbing substance. The mixture to be separated is added at the top of the column where all the substances are absorbed. A solvent is passed through the column and the substances most strongly held remain in a layer near the top while those less strongly absorbed form successive layers down the column. By continued washing, the substances may be made to descend one by one through the bottom of the column. This method has been studied by Schwab and Jockers[41] for the separation of inorganic cations on adsorbents like aluminum oxide. Analogous procedures can be used with zeolites as adsorbents and solutions of ions as the solvent.

A counter current system similar to that of a counter flow column with total reflux at both ends can be simulated as follows. The column can be filled with a zeolite having an easily replaceable cation compared to the isotopic ions. A quantity of a salt containing the isotopic ions is then added at the top of the column. Following this is a solution containing a cation very strongly held to the zeolite such that practically all the isotopic ions are replaced and descend down the column. The net result will be that effectively the quantity of zeolite containing the isotopic ions moves down the column with reflux at the leading and tailing end.

Experiments on the Fractionation of the Lithium Isotopes

Determination of the fractionation factor

In order to determine the possible effectiveness of the base exchange reactions in separation of the isotopes, a determination of the fractionation factor was made. It is given by the ratio $Li^6Z : Li^7Z/Li^{6+} : Li^{7+}=\alpha$, that is, the distribution of the isotopes between the two phases. If α were large enough, a single stage equilibrium could be used for its determination. However, it is small in most isotopic exchange reactions and thus the single stage must be multiplied many times. The method chosen was to extract a large quantity of

[37] Austerweil, Bull. Soc. Chem. France **51**, 732 (1932).
[38] Hunter and Nash, J. Ind. Eng. Chem. **27**, 836 (1935).
[39] Zechmeister and Cholnoky, *The Chromatographic Adsorption Method* (Springer, Austria, 1937).
[40] Lederer, Chemie and Industrie **33**, 1072 (1932).
[41] Schwab and Jockers, Angew. Chemie **50**, 546 (1937).

lithium chloride solution with successive small quantities of sodium zeolite so that α is approximately given by the Rayleigh distillation formula,

$$\left(\frac{1-N_0}{1-N}\right)^{1/(\alpha-1)}\left(\frac{N}{N_0}\right)^{\alpha/(\alpha-1)}=\frac{W_0}{W},$$

where N_0 is the mole fraction of the heavy isotope in the initial amount of material W_0, and N the mole fraction in the final amount of material W. A batch containing 300 g of lithium chloride in a 20 percent solution was extracted with a large number of successive 30 g portions of sodium zeolites. The zeolite was a synthetic one called "Decalso" and kindly furnished by the Permutit Company for this research. It had a calculated exchange capacity of about 0.32 equivalents per 100 grams and was graded by Tyler screens from 40 to 60 mesh. After each addition the mixture was shaken vigorously for twenty minutes before filtration. At various intervals the sodium chloride resulting from the replacement of the sodium ion from the zeolite was separated from the remaining lithium. When the amount of lithium had been reduced by a factor of 70, the ratio of the isotopes in the remaining solution was determined. These experiments were made before our mass spectrometer was constructed and the samples were kindly analyzed by A. Keith Brewer and later checked. The ratio of $Li^7 : Li^6$ had changed from 11.6 to 12.7. Substitution in the Rayleigh formula gives 1.022 for the fractionation factor. It is difficult to estimate the accuracy or exact meaning of this value because of the variable concentration of lithium and sodium ions, and because the Rayleigh formula does not apply very closely towards the end of the extraction where the quantities of zeolite added were comparable to the amount of lithium remaining. However, the value does give us a fair approximation to what one can expect in a column since somewhat similar conditions occur.

The reverse procedure was also tried in which 2 kg of lithium zeolite were extracted with 36 successive liters of 2 percent chloride solution. The lithium extracted by the last batches of solution showed a ratio of the isotopes of 10.7 which gives a fractionation factor of 1.023 calculated as above.

Experiments on zeolite columns

As pointed out previously, one of the most convenient ways of multiplying the single stage effect is the use of a column of zeolite. A number of preliminary experiments were made to determine if possible the best procedure and conditions for a fractionation. It was not known, for example, whether dilute or concentrated solutions would be more advantageous. One form of the zeolite may be more effective than another. Thus, the use of a more stable zeolite like potassium or barium in place of a sodium zeolite may possibly be better since this would afford more competition for the two isotopes. The possible significance of the rate of diffusion or reaction during exchange was not known. The operation of the column would be different if the rate of extraction or adsorption rather than some equilibrium process were the controlling mechanism. The answers to all these questions have not yet been determined, but the following experiments do give us some ideas as to the nature of the fractionation process.

The first column constructed was a three-quarter inch stainless steel pipe thirty-five feet long packed with about 2 kg of sodium zeolite. The second column was made of a one and one-quarter inch hard rubber pipe thirty feet long containing about 4 kg of sodium zeolite. A third column of one and one-quarter inch hard rubber pipe one hundred feet long was constructed in one of the stairwells of the Chandler Chemical Laboratory. This was filled with about 13 kg of sodium zeolite furnished by the Permutit Company. These columns will be referred to as *A*, *B*, and *C*, respectively. In all cases care had to be taken to make sure that no air bubbles or pockets were left in the column. The most convenient way to fill the column was to fill each ten-foot section as it was added. The section was filled with water and the wet zeolite poured in, the water displaced being drawn off by suction. Tees fitted with one-quarter inch outlets were placed between each section so that samples could be taken. The velocity of the liquid flow was regulated by pinch clamps on heavy pressure tubing at the bottom. The solutions were fed by

TABLE I. *Result on fractionation of lithium isotopes.*

EXPERIMENT	COLUMN	FORM OF ZEOLITE	SOLUTION AND PROCEDURE	SAMPLE OF Li THROUGH COLUMN	RATIO Li^7/Li^6 NORMAL RATIO 11.7
1	*A*	NaZ	3% LiCl passed through	Leading	13.3±0.3
2	*A*	NaZ	1% LiCl passed through	Leading	12.5
3	*A*	NaZ	1% LiCl passed through	Leading	12.3
4	*B*	NaZ	15 g LiCl washed down with 0.5% NaCl	Leading Tailing	12.6 8.9
5	*C*	NaZ	15 g LiCl washed down with 3.0% NaCl	Leading Tailing	14.1 8.8

inverting a large bottle over the top of the column. When the liquid ran below the level of the outlet tube in the bottle, air entered the bottle and more liquid ran out, thus maintaining a fairly constant level.

The samples used for analysis of the isotope ratio were evaporated just to dryness and extracted with amyl alcohol. A little P_2O_5 was added to the lithium chloride and put on a platinum disk in the form of a paste. After heating to redness on a tungsten filament for ten to fifteen minutes under vacuum, the disk was cleaned and spot welded to the filament of the mass spectrometer and the ratio of the isotopes determined as previously described. The results reported are the average taken from eight to fifteen determinations.

The results for a number of experiments with lithium are given in Table I.

In experiments 1, 2, and 3 the column was initially full of distilled water and sodium zeolite. The lithium chloride was allowed to run in at the top at a rate of about 2 to 3 cc per minute. Tests were made at intervals on a spectroscope to determine when the first lithium came through the bottom of the column. The first lithium through was taken as the leading sample and was analyzed on the mass spectrometer as described above. About one-half the replaceable sodium in the column was exchanged before the first lithium appeared. Experiments 2 and 3 were made to test the effect of concentration, but the very first lithium coming through was missed in both of these and therefore the results do not necessarily show the influence of dilution. A receiver system was used thereafter which allowed the effluent to successively fill 200 cc bottles. Between each experiment the zeolite had to be completely regenerated by passing sodium chloride solution through the column.

Experiments 4 and 5 were carried out according to the methods of chromatographic analysis. The columns were initially filled with sodium zeolite and with the same solution which was to be used for washing down the lithium chloride. The charge of lithium chloride was added at the top of the column in a fairly concentrated solution (10 percent) and the sodium chloride solution was allowed to run in at the rate of about 2–3 cc per minute. The first lithium appearing was taken as the leading sample and the last to come through as the tailing sample. In experiment 4 about 70 g of sodium chloride in a 0.5 percent solution were required before the first lithium came through the column. Experiment 5 was made with the 100 foot column during an experiment on potassium. We had expected much more change than was obtained. The 3 percent sodium chloride washed the lithium through the column rather rapidly. A more dilute solution would probably have given better results. Further experiments are being made to test this point. All of the solution coming through the column was saved and samples were analyzed to determine the isotope ratio and the total amount of lithium coming through up to the time of the sample. The amount of lithium was determined by the spectroscopic method.[42] While this method of analysis does not give results to better than 5 percent to 10 percent, this accuracy is sufficient to show the variation in isotope ratio as the lithium comes through the column. Such a curve will give us an estimate of the quantities of changed material which can be expected by this procedure. A curve for experiment 5 is given in Fig. 1.

In all the experiments on lithium, the leading sample had a lower concentration of Li^6 while the tailing sample had a higher concentration. This means that Li^{6+} is preferentially taken up by the zeolite and is not so readily removed as Li^{7+}.

[42] Skinner and Collins, U. S. Dept. of Agri. Bull. Chem. 153.

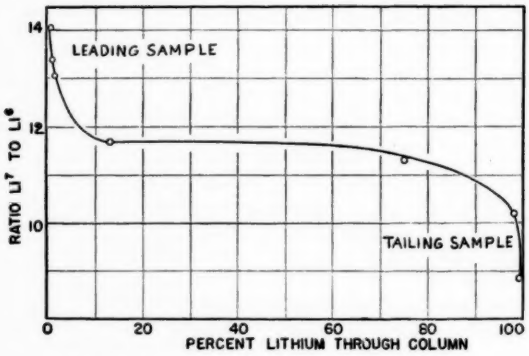

FIG. 1. Distribution of lithium isotopes coming through column in experiment 5.

EXPERIMENTS ON THE FRACTIONATION OF THE POTASSIUM ISOTOPES

The same general procedures as those used for the lithium isotopes were tried for potassium and for the nitrogen isotopes in NH_4^+. A fractionation of the potassium isotopes with sodium zeolite was found to be more difficult especially in regards to the leading sample. This may possibly be due to the great difference in the binding of the lithium and potassium to the zeolite. Most of the preliminary experiments were made to see whether or not a change could be made on the leading sample.

The solution coming through the column was tested for potassium with sodium cobaltinitrite. When its presence was shown by this test, a quantity of the liquid was evaporated and the potassium precipitated as the cobaltinitrite. This was, decomposed by heating, and after filtering off the cobalt oxide, the sodium and potassium nitrites were converted to the chlorides. A little P_2O_5 was added and the ratio of the isotopes determined as described for lithium. The presence of sodium did not interfere with the analysis.

Table II shows the results of a number of the experiments.

In experiment 1 the 1 percent KCl solution was passed through the column of sodium zeolite at the rate of about 2 to 3 cc per minute. About three-fourths of the calculated replaceable sodium was exchanged before potassium came through in sufficient quantities to give a test with cobaltinitrite. No change was found in the leading sample, but after washing the potassium from the column with about forty liters of 5 percent sodium chloride solution, the ratio of K^{39} to K^{41} was found to be 13.4. For experiment 2, the column was converted to calcium zeolite, filled with water, and a 3 percent potassium chloride solution started through as before. When sufficient potassium had come through to give a test with cobaltinitrite the ratio was 14.2 showing no significant change. However, about five liters of the first solution through the column was saved and later evaporated to recover any potassium. The small amount obtained (about 20 mg of $K_2NaCo(NO_2)_6$) was analyzed and found to have increased in ratio to 14.8.

Experiment 3, using 0.5 percent KCl instead of 3 percent KCl, showed no marked advantage in using more dilute solutions. However, under conditions where an appreciable fractionation is obtained, the more dilute solutions may yet prove to be more effective. The equilibrium constants as given by Eq. (1), or the constants from other equations,[3] are generally about twice as large for replacement of ions from a zeolite by K^+ as for Na^+. It was thought that a mixture containing two equivalents of sodium chloride to one of potassium chloride when passed down the column may give a better fractionation. Accordingly for experiment 4, the column was filled with sodium zeolite and 0.30 *N* NaCl solution. A mixture of 0.15 *N* KCl and 0.30 *N* NaCl was then started through. The leading sample again showed no significant change in isotope ratio. Experiments made in this manner using sodium or calcium zeolites apparently will not give large changes in the ratio of the potassium isotopes in the leading sample.

Experiment 5, carried out according to the methods of chromatographic analysis, gave no significant change in the leading sample, but the tailing sample was changed to a ratio of 12.9. The same experiment was tried on the 100 foot column but the potassium spread throughout the whole column so much during the passage of the 3 percent sodium chloride solution that the experiment was finally stopped when the ratio of the potassium isotopes in a sample taken from the top section of the column was 13.2. The use of larger quantities of potassium chloride and higher concentration of sodium chloride may have been better. Further experiments will be made later. The experiment using a column of sodium zeolite

and a solution of barium chloride to follow the potassium down shows some promise since a change was observed in both the leading and tailing samples. The use of ammonium zeolite and ammonium ion which is similar to potassium in replacing power may also prove more effective than the sodium zeolite.

In all those experiments in which a change in the ratio of the potassium isotopes was obtained, K^{41} was decreased in the leading sample and increased in the tailing sample. It seems, therefore, that the heavier isotope is taken up more readily by the zeolite and is more difficult to replace. This is the opposite of the effect observed for lithium.

Experiments on the exchange of ammonium ion with a sodium zeolite and a carbonacious zeolite given to us by the Permutit Company showed a small change in the isotope ratio in the same direction as observed for potassium, i.e. the heavier isotope was more readily taken up by the zeolites. The analyses were made on a mass spectrometer by Marvin Fox in this laboratory.

TABLE II. *Experiments on fractionation of potassium and nitrogen isotopes.*

EXPERIMENT	COLUMN	FORM OF ZEOLITE	SOLUTION PASSED THROUGH COLUMN	SAMPLE OF K THROUGH COLUMN	ANALYSIS $K^{39}:K^{41}$ 14.10
Potassium 1	*A*	NaZ	1% KCl passed through	Leading	14.1±0.2
1*a*	*A*	KZ	5% NaCl passed through	Tailing	13.4
2	*A*	CaZ_2	3% KCl passed through	Leading (*a*) Leading (*b*)	14.8 14.2
3	*A*	CaZ_2	0.5% KCl passed through	Leading	14.2
4	*A*	NaZ	0.15 NKCl +0.30*N* NaCl	Leading	14.1
5	*B*	NaZ	100 g KCl washed down with 5% NaCl	Leading Tailing	14.3 12.9
6	*C*	NaZ	100 g KCl washed down with 3% then 5% KCl	—	13.20
7	*B*	NaZ	15 g KCl washed down with 1 *M* $BaCl_2$	Leading Tailing	14.6 13.5
Nitrogen 1	(NH^+_4) *A*	NaZ	2% NH_4Cl passed through	Normal Leading	$N^{14}N^{14}$: $N^{14}N^{15}$ 124.3 136.8
2	8 ft.	HZc	1% NH_4Cl passed through	Normal Leading	127.4 130.8

DISCUSSION

The fractionation of the isotopes by this method depends upon a difference in binding of the two isotopic ions with water and with the zeolite. The differences are due to a difference in the zero point energies and the vibrational and rotational frequencies of the two isotopic combinations in much the same way as those calculated for gaseous systems by Urey and Greif[1] and demonstrated experimentally for the liquid-gas chemical exchange systems previously referred to. Solvation of the ions and the specific nature of the zeolite are, therefore, important considerations. Any change in the system affecting the nature of the solvent medium will affect the binding of the two isotopic ions, and if this is not in the same ratio for the solvation and binding of the ions to the zeolite, there will be a change in the effectiveness of the fractionation. We cannot predict whether it would improve or decrease the desired fractionation, nor can calculations be made for such a complicated system. Thus far we have studied the fractionation with only one or two forms of the same zeolite and have not markedly changed the nature of the solvent medium. Other types of zeolites such as the bentonite clays, the natural "greensands" or the newly developed organic exchange resins are to be studied. Addition of alcohol or other solvent may also influence the fractionation obtained.

If the process by which the isotopes are fractionated is an equilibrium one, we may write the following equations:

$$Li^{6+}+NaZ \leftrightarrows Li^{6}Z+Na^{+}$$

$$\underline{Li^{7+}+NaZ \leftrightarrows Li^{7}Z+Na^{+}}$$

$$Li^{6+}+Li^{7}Z \leftrightarrows Li^{7+}+Li^{6}Z \qquad K=1.022.$$

Similarly

$$K^{39+}+K^{41}Z \leftrightarrows K^{41+}+K^{39}Z \qquad K<1$$

$$N^{14}H_4^{+}+N^{15}H_4Z \leftrightarrows N^{15}H_4^{+}+N^{14}H_4Z \qquad K<1.$$

The lighter lithium isotope is preferentially taken up by the zeolite while the reverse is true for the potassium and ammonium ions. The process responsible for the fractionation is essentially an equilibrium one rather than one due to differences in the rate of diffusion or reaction,

since otherwise the lighter isotopes would all diffuse faster resulting in changes of the isotope ratio in the same direction. In those experiments in which lithium chloride solutions were passed through the column filled with sodium zeolite, differences in the rate of diffusion of the two isotopic ions would tend to decrease the concentration of Li^6 and therefore increase the fractionation in the leading sample. If diffusion or rate of reaction were the important process, the tailing sample produced by passing sodium chloride solution through a column of lithium zeolite should also give a solution containing a higher concentration of Li^7 since Li^6 should diffuse out of the zeolite faster. This is not the case. In those experiments made according to the procedures of chromatographic analysis, the decrease of Li^6 in the leading sample is approximately the same as the increase of Li^6 in the tailing sample.

The experiments are not yet extensive enough to draw definite conclusions as to which method is the most effective procedure. The procedure according to the methods of chromatographic analysis will give samples with both higher and lower amounts of Li^6. However, if a change is desired in one direction, it seems that the first procedure should be better. That is, to obtain a higher concentration of Li^6, the column should be converted to lithium zeolite and sodium chloride solution slowly passed in at the top so as to displace the lithium from the zeolite. The sodium ion replaces Li^{7+} more readily than the Li^{6+} such that the last lithium replaced from the column has a higher concentration of Li^{6+}. Since there is a distribution of the lithium between the two phases following the laws previously described, one may obtain the number of stages by methods similar to those used in extraction problems. By assuming the number of effective isotopic exchanges is the same as the number of stages thus determined, it is possible to calculate the separation which can be expected once the fractionation factor is known.

Acknowledgments and thanks are due Dr. A. Keith Brewer for his suggestions and advice in construction of the mass spectrometer and for some of the analyses during the first part of the investigation. Thanks are also due Dr. John G. Dean and the Permutit Company for the zeolites used in the research.

Summary

1. The methods used in fractionation of the lithium and potassium isotopes have been discussed and some additional results on the electrolysis of lithium chloride reported.

2. The properties of zeolitic substances significant in studies on the separation of isotopes by chemical exchange are described.

3. The natural abundance ratio of the lithium and potassium isotopes have been determined by analysis on the mass spectrometer and compared to the values reported in the literature. The average value obtained for the ratio $Li^7 : Li^6$ was 11.71 ± 0.14 and for $K^{39} : K^{41}$ was $14.10 \pm .09$.

4. The fractionation factor for the lithium isotopes in the exchange with sodium zeolite was found to be 1.022.

5. A fractionation of the lithium, potassium and nitrogen isotopes using long columns filled with zeolites has been effected. Both an increase and decrease of about 25 percent from the normal abundance ratio of the lithium isotopes has been obtained. A change of about 10 percent has been obtained for the potassium and nitrogen isotopes.

6. Some of the factors involved in the mechanism of the process are discussed.

Kinetics of OH Radicals as Determined by Their Absorption Spectrum

III. A Quantitative Test for Free OH; Probabilities of Transition

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(1) In order to make the OH absorption bands applicable to a *quantitative* chemical test for free OH their probability of transition (f value) was measured by the concentration of "dispersion electrons" in a known concentration of OH. (2) This concentration of OH is produced by water vapor dissociated at 1473°C, the equilibrium of which was computed. (3) The concentration of the "dispersion electrons" was measured by photometry of the absorption lines photographed with high resolving power. (4) The f values of the various absorption lines are given in a table. The most intense lines have f values of the order of magnitude 2×10^{-4}. The accuracy is estimated to be 15 percent, the sensitivity (smallest detectable pressure under the conditions of the present experiment) 0.01 mm. (5) Comparison with other f values leads to the conclusion that the OH absorption band belongs to a half-forbidden transition. The lifetime of the excited state is computed as approximately 4×10^{-6} sec.

I. PROBLEM

IN preceding papers[2–6] the absorption spectrum was applied as a chemical test for free hydroxyl radicals in gases. The purpose was to investigate some phases of the kinetics of the hydrogen-oxygen reaction, in particular to trace the progress of a fast reaction by snapshots. First, a *qualitative* test for OH was made in low pressure H_2O vapor, after interrupting an electric discharge which is known to dissociate H_2O into H and OH. The next step was a *quantitative* test in the *relative* sense in which the rotational lines, on the basis of the known thermal distribution of rotation, served as "concentration marks" to indicate the relative values of the hydroxyl concentration. This test was carried through by Frost and Oldenberg for various values of pressure. The result was that the rate of disappearance of OH increases with pressure and one infers that triple collisions are required for the reaction by which OH is consumed. In order to measure the rate constant of this reaction a *quantitative* test in the *absolute* sense had to be carried through. For this purpose the observed absorption spectrum of OH had to be calibrated against a known value of OH concentration which can be produced only by thermal dissociation of H_2O vapor into H+OH. This equilibrium was discovered and measured at temperatures between 1260 and 1590°C by Bonhoeffer and Reichardt.[7] For the purpose of this calibration, in the present paper, the *absolute* intensities of the absorption lines of OH, in thermally dissociated water vapor, are investigated by photographic photometry, and from these measurements their transition probabilities are computed or, in the conventional expression, their "f values" are determined.

Apart from the importance of the f value as leading to a quantitative test for free hydroxyl, such an investigation is of interest from the purely spectroscopic point of view. Although f values have been determined for many *atomic* absorption lines, very little is known about the f values of *molecules* (see Section VIa).

These f values apply also to problems of the solar spectrum. The presence of molecules in the

[1] The experiments reported in this paper were performed in 1936 (J. Phys. Chem. **41**, 293 (1937); Phys. Rev. **51**, 381 (1937)). The detailed computation was postponed in order to apply more accurate values of the equilibrium constants. In the meantime such values have been published by H. Zeise, Zeits. f. Electrochem. **43**, 704 (1937) and are applied in the present paper. For help in the preparation of the experiments reported here, we wish to express our appreciation to Dr. Martin Grabau.

[2] O. Oldenberg, J. Chem. Phys. **2**, 713 (1934) and **3**, 266 (1935).

[3] A. A. Frost and O. Oldenberg, J. Chem. Phys. **4**, 642 (1936).

[4] A. A. Frost and O. Oldenberg, J. Chem. Phys. **4**, 781 (1936).

[5] A. A. Frost, D. W. Mann, O. Oldenberg, J. Opt. Soc. Am. **27**, 147 (1937).

[6] O. Oldenberg and F. F. Rieke, J. Chem. Phys. **6**, 169 (1938).

[7] K. F. Bonhoeffer and H. Reichardt, Zeits. f. physik. Chemie **A139**, 75 (1928).

FIG. 1. Absorption experiment. *A*, absorption tube; *F*, high temperature furnace; *B*, *C*, *D*, auxiliary furnaces to prevent condensation; *Q*, quartz plates; *T*, constant temperature both; *S*, stirrer; *f*, porous filter.

solar atmosphere has been discussed by Russell[8] on the basis of their absorption bands. Russell based his estimates of concentration on the picture of an atmosphere of mean temperature and pressure for which he computed the thermal equilibrium. It is expected that the *f* values reported here will make possible a far more direct determination of the total concentration of OH in the solar atmosphere.

Finally, these *f* values are of interest because they yield a value for the lifetime of the excited state of OH. In preceding papers *collisions during the lifetime* were discussed as explaining the intensity distribution of OH bands excited in an electric discharge through H_2O with various amounts of He added. The value of the lifetime determined here leads to an estimate of the efficiency of such collisions (Section VIb).

The OH bands, in spite of their complicated structure of twelve branches, are suitable for an investigation of their intensities since, on the basis of the theory of Hill and Van Vleck,[9] the intensity relations between the various branches are well known.

The probability of transition, that is, the "*f* value," is a constant characteristic for each single line. It is determined as the number per cc of "dispersion electrons" (derived from the intensity of the absorption line) divided by the number of OH radicals able to absorb this individual line (derived from the thermal equilibrium). The determination of these two quantities will be discussed in the following sections.

[8] H. N. Russell, Astrophys. J. **79**, 317 (1934).
[9] E. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928). The general formulae have been adapted to the special case of OH by L. T. Earls, Phys. Rev. **48**, 423 (1935).

II. Concentration of the Initial State of Absorption

(a) Experiment

As discovered by Bonhoeffer and Reichardt, water vapor is thermally dissociated—in addition to the well-known process $2H_2O \rightleftarrows 2H_2+O_2$ (equilibrium constant $K(O_2)$)—by the process $2H_2O \rightleftarrows H_2+2OH$ (equilibrium constant K_{OH}), both equilibrium constants being of the same order of magnitude.

In order to make the absorption spectrum of OH observable with a medium-size quartz spectrograph, Bonhoeffer and Reichardt produced a comparatively high degree of dissociation by a temperature as high as 1590°C. Our purpose has been to investigate smaller concentrations of OH in electric discharges with an instrument of higher sensitivity, that is, to observe individual absorption lines with a spectrograph of far higher resolving power. Hence for the calibration a lower temperature was sufficient to dissociate the water vapor partially.

The absorption tube, *A* (Fig. 1), 110 cm long and 4.6 cm wide, made of "Pythagoras composition" was used.[10] Short glass tubes with side tubes for inlet and outlet and with plane flanges were cemented on the ends. Plane quartz windows, *Q*, were pressed against the flanges by springs. It was not necessary to make them vacuum tight since the vapor in the tube had a slight excess pressure. A furnace, *F*, 50 cm long, wound with Nichrome V wire, covered the middle section of the tube. This oven could be heated without difficulty for many hours to 1200°C. The temperature distribution along the axis of the oven was measured with a Pt/Pt-Rh thermocouple, calibrated against the melting point of Cu. The Cu sample was furnished by the National Bureau of Standards.

Since pure water vapor under the conditions described gives only weak absorption lines, the mixture $\frac{2}{3}H_2O+\frac{1}{3}O_2$ was applied; this mixture, containing equal numbers of H and O atoms, gives a maximum concentration of OH. The mixture was prepared largely as described by Bonhoeffer and Reichardt. In order to secure saturation of the oxygen, bubbling through

[10] Manufactured by W. Haldenwanger, Spandau, Germany.

water at 89°C, very small bubbles were produced by passing the oxygen through a fine porous filter, *F*. The resulting mixture, after passing through the absorption tube, was analyzed. One can easily derive from the mass action law that the composition of the mixture is not critical since the dissociation yielded by the mixture described represents a maximum.

(b) Computation

(α) *Pressure of OH.*—The total pressure of the mixture studied must be one atmosphere, for technical reasons. For a given total pressure the maximum value of p_{OH} occurs, according to Bonhoeffer and Reichardt, when $p(H_2O)=2p(O_2)$. Since the degree of dissociation is very small at the temperatures used in our experiments, the pressure $p(O_2)=\frac{1}{3}$ atmos. and $p(H_2O)=\frac{2}{3}$ atmos. can be considered as constant. Then p_{OH} follows from

$$\frac{K_{OH}^2}{K(O_2)}=\frac{27}{4}\cdot\frac{p_{OH}^4}{(1-p_{OH})^3},$$

where $K(O_2)$ and K_{OH} are functions of the temperature (p_{OH} in atmos.). In our case p_{OH} is so small (1/2000 atmos.) that in the denominator p_{OH} is negligible as compared to 1.

While the values of $K(O_2)$ as a function of temperature are well known, the values of K_{OH} are less certain, largely because the energy of dissociation of H_2O into H+OH is not known with sufficient accuracy.[11] We applied the most recent values published by Zeise[12] which do not differ much from the results of Bonhoeffer and Reichardt.

The temperature distribution along the axis of the furnace was determined with the thermocouple, the corresponding distribution of p_{OH} was computed and, by graphical integration, an equivalent value of $p_{OH}=0.35$ mm was determined, which, over a tube length of 44 cm would represent the same absorbing layer. The number of OH per cc follows from the kinetic theory.

(β) *Population of the individual initial states.*—The energy levels of OH were computed from the band spectrum as analyzed by Fortrat[13] on the basis of the energy level diagram for $^2\Sigma-\Pi^2$ bands. The rotational terms of the lowest electronic term are given in Table I, neglecting Λ type doubling, which is only of the order of magnitude of a few cm^{-1}. By the Boltzmann formula the thermal distribution was determined over both electronic levels $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{1\frac{1}{2}}$, the various rotational levels, and the vibrational levels $v=0$ and $v=1$. (The term $v=1$ (3568 cm^{-1}) contributed only three percent and $v=2$ was negligible.) The Λ type doubling is so small as compared to kT that, for the computation of the thermal distribution it can first be neglected and finally taken into account by assuming that all levels split into doublets of equal statistical weight. (In this computation of the thermal equilibrium it was assumed that no more low electronic levels exist which may be unknown, since they fail to emit bands in the easily accessible spectral range. Such unknown levels would reduce the population of the levels considered here.) The result of this computation was the population N_{rad} per cc of OH radicals of any initial state for which the absorption intensity was measured.

III. Concentration of Dispersion Electrons

(a) Experiment

For the measurement of the intensity of individual absorption lines the light traversing the absorption tube described had to be analyzed with a spectrograph of a resolving power higher than the width of the lines. Here a major experi-

Table I. *Rotational terms (cm^{-1}) of the lowest electronic term of* OH.

J	$^2\Pi_{\frac{1}{2}}$	$^2\Pi_{1\frac{1}{2}}$	J	$^2\Pi_{\frac{1}{2}}$	$^2\Pi_{1\frac{1}{2}}$
$\frac{1}{2}$	138		$9\frac{1}{2}$	2068	1656
$1\frac{1}{2}$	199	0	$10\frac{1}{2}$	2464	2021
$2\frac{1}{2}$	300	84	$11\frac{1}{2}$	2895	2421
$3\frac{1}{2}$	441	203	$12\frac{1}{2}$	3360	2855
$4\frac{1}{2}$	620	356	$13\frac{1}{2}$	3858	3321
$5\frac{1}{2}$	836	545	$14\frac{1}{2}$	4388	3821
$6\frac{1}{2}$	1090	770	$15\frac{1}{2}$	4951	4354
$7\frac{1}{2}$	1380	1030	$16\frac{1}{2}$	5544	4918
$8\frac{1}{2}$	1706	1325	$17\frac{1}{2}$	6168	5514

[11] See A. R. Gordon, J. Chem. Phys. **1**, 311 (1933).
[12] See reference in footnote 1 and B. Lewis and G. von Elbe, J. Chem. Phys. **3**, 63 (1935).
[13] Fortrat, J. de phys. **5**, 20 (1924). W. Jevons, *Report on Band Spectra of Diatomic Molecules* (The Physical Society, Cambridge, 1932), p. 164.

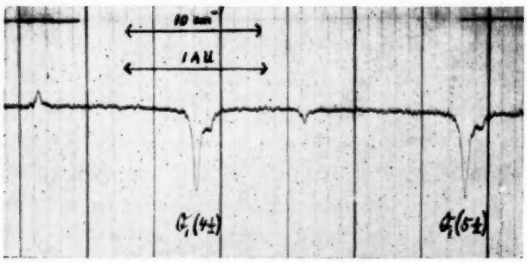

FIG. 2. Section of densitometer trace.

mental difficulty arose because of the small width of the OH absorption lines. We could not increase their width by pressure broadening, as Füchtbauer did for alkali lines, for that would have required a pressure of many atmospheres—too difficult a problem to handle for high temperatures and a large volume.

The second order of a 21-foot concave Rowland grating, mounted at this laboratory by Dr. F. H. Crawford and Mr. D. W. Mann, proved sufficient for the present purpose. The intensity of illumination was increased by a factor of about 16 by a cylindrical quartz lens in front of the photographic plate. A lens 5×5 cm^2 is large enough to cover the Q_1 and Q_2 branches of the OH band which, because of their high intensity, best lend themselves to observation. Eastman IV−O plates were used because of their fine grain and high contrast, both properties being of the greatest importance for the investigation of narrow and faint absorption lines; their very low speed was not a serious obstacle because of the gain of intensity by the cylindrical lens. The continuous spectrum of hydrogen served as a background. The hydrogen discharge tube was developed for the purpose of these investigations by Dr. N. D. Smith.[14] Fig. 2 shows a small section of the densitometer trace.

(b) Computation

The classical electron theory attributes the integrated absorption coefficient of a single observed absorption line to the number per cc N_{el} of vibrating "dispersion electrons." This number is derived from the absorption measurements as follows: For each frequency within the line the intensity transmitted is given by $i(\nu)=i_0\cdot e^{-\alpha_\nu l}$ (i_0=uniform incident intensity of background; ν=frequency in cm^{-1}; α=absorption coefficient per unit length; l=length of absorbing layer). From the densitometer curve i/i_0 is derived as a function of ν and α_ν is computed. The number of dispersion electrons characteristic for this line is

$$N_{el}=\frac{mc^2}{\pi e^2}\int_0^\infty \alpha_\nu d\nu$$

(m=mass of electron; e=charge on electron in e.s.u.; c= velocity of light).[15]

$\int_0^\infty \alpha_\nu d\nu$ was derived from the densitometer traces by the following procedure. The $Q_1(6\frac{1}{2})$ line has only a weak satellite. For this line the logarithm of the ratio i_0/i was plotted against the wave number and the area under the curve taken as the quantity $l\int_0^\infty \alpha_\nu d\nu$. However, the remaining lines are in more complex groups which must be resolved by graphical methods in order to yield the above integral for each line of the group. Since the absorption coefficients for overlapping lines are additive, the graphical separation into component lines was conveniently carried out with a plot of log i_0/i against ν. The contour of the $Q_1(6\frac{1}{2})$ line was taken as a standard. By trial and error, lines of this shape were given separations and heights which would add to fit the observed contour of the group. The actual computation is simplified because in the range of photographic densities used, the relation between density and log I is accurately represented by a straight line. In this case, log I varies linearly with log d where d is the galvanometer deflection read from the microphotometer trace. The above procedure may be carried out with plots of log d against positions along the trace, and the areas derived for the individual lines converted to give $l\int_0^\infty \alpha_\nu d\nu$ by means of a constant multiplier which involves the contrast of the photographic plate and the dispersion on the trace. Typical contours are illustrated in Fig. 3.

[14] N. D. Smith, J. Opt. Soc. Am. **28**, 40 (1938).

[15] This formula follows from the one applied by Füchtbauer, Joos and Dinkelacker (Ann. d. Physik **71**, 222 (1923)), when one considers that their q is identical with $i(\nu)/i_0$; hence $4\pi nkl/\lambda$ is identical with $\alpha_\nu l$. We applied cm^{-1} instead of Füchtbauer's sec.$^{-1}$.

For frequencies of the OH band considered and with a length of 44 cm of the absorbing layer the result was

$$N_{el} = 2.54 \times 10^{10} \times l \int_0^\infty \alpha_\nu d\nu (\text{cm}^{-3}).$$

IV. Results

(a) Uncorrected; correction for lack of resolving power

The numerical results are given in Table II. Column I gives the line observed. The lines belong to the branches Q_1, R_2, P_1, and ${}^QP_{21}$. Column II gives the integrated absorption coefficient $l\int \alpha_\nu d\nu$, derived from the photometry of the absorption lines, as it is needed for the computation of the number of dispersion electrons. These integrals may be considered as expressing line intensities.

The values of column II indicate by a systematic defect that a correction must be applied. The outstanding difficulty in the measurement of the intensities of narrow absorption lines is due to lack of resolving power. This is evident from the limiting case, the complete disappearance of absorption lines in spectrographs of poor resolving power. The intensities of such lines can be measured only with a spectrograph of a resolving power considerably higher than the width of the lines. Technically it seems possible to approach this condition reasonably well for the OH bands in the furnace. The resolving power of the grating in the second order is, theoretically, 0.145 cm^{-1}. It seems hardly possible to apply a still higher resolving power. The third-order grating spectra have so much less intensity that they cannot very well be used in this experiment. Furthermore, Fabry-Pérot plates or similar instruments of highest resolving power cannot be used for absorption spectra with a continuous background because of the very close proximity of adjacent orders. The Rowland grating at our disposal is supposed to have a resolving power nearly equal to its theoretical value of 0.145 cm^{-1} as tested in investigations on band spectra and Zeeman effects. It was used with its full aperture as the knife-edge method failed to reveal deficiencies of any zones. On the other hand the observed line width of OH in the furnace was 0.58 cm^{-1}, that is, four times the resolving power.

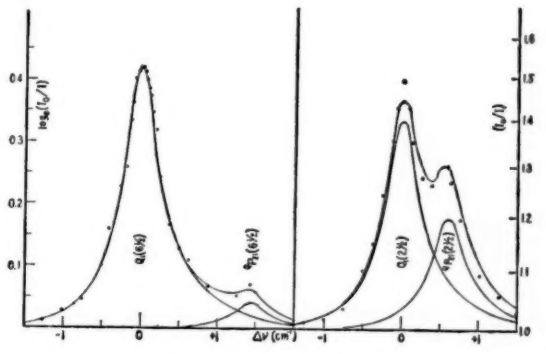

FIG. 3. Intensity curves.

Obviously it is desirable to check whether the results were affected by a lack of resolving power. First we applied the method of Slater [16] by which the contour of a line may be corrected for the lack of resolving power. We assumed that the actual resolving power was given by the theoretical resolving power of the grating and the slit width applied at the densitometer. This procedure resulted in a correction of at most a few percent at the center of the absorption coefficient contour.

However, a second method yielded corrections so much larger that we were led to the conclusion that the over-all resolving power is considerably less than we had assumed. Without extensive tests it is impossible to decide if the discrepancy lies in the grating, the densitometer, or in the inability of the photographic-plate to reproduce accurately steep intensity gradients[17] (the half-value width of the lines measures only 0.06 mm on the plate). The second method was a modification of the one applied by Bourgin[18] in his work on the intensity of infra-red absorption spectra. The eventual error was expected to be larger the steeper the line contour, that is,

[16] J. C. Slater, Phys. Rev. **25**, 783 (1925).

[17] The "Eberhard effect" is expected to be appreciable only for densities higher than 1 (*Handbuch der Experimentalphysik*, Vol. 26, p. 693); our background density was about 0.7; the plate was brushed during development. The resolving power of the Eastman IV–0 plate is estimated at 1/85 mm using white light. Using ultraviolet light, it is probably 1.5 or 2 times as great. Judged by these figures, the plate should reproduce the contour of a line, 0.06 mm wide, quite well.

[18] D. G. Bourgin, Phys. Rev. **29**, 794 (1927).

the more abrupt the change of intensity with frequency. Bourgin took this error into account by varying the depth of the absorbing layer. For ideal resolving power the intensity (integrated absorption coefficient) per unit length ought to remain constant. Actually the long tube yielded an apparently smaller intensity per unit length because the spectrograph failed to show the steeper line contour. The absorption line seemed to be too shallow. In order to obtain a correction factor, Bourgin plotted the observed intensity per unit length against the observed total intensity. He extrapolated this curve for smaller intensities and thus determined the corrected value as the limit for zero tube length.

In our case of the OH bands, we could not easily vary the tube length. But, instead, we could predict the various intensities of single lines, on the basis of the theory of Hill and Van Vleck, in conjunction with the populations of the various initial states determined in Section IIb(β). Actually the observed intensities given in Table II, column II, failed to come in the ratios theoretically predicted; there was a *systematic* deficiency of the more intense lines. By plotting the ratio (intensity observed)/(intensity predicted) against the intensity predicted (Fig. 4) a straight horizontal line was not actually obtained, as would be expected for ideal resolving power. Instead, the line had a definite slope which indicated that the observations were too small for the strongest absorption lines, as is characteristic for lack of resolving power. The line was reasonably smooth and straight and covered so wide a range of intensities that a minor extrapolation led to the limiting value for zero intensity. (If, instead, the ratio (intensity observed)/(intensity predicted) was plotted against the rotational quantum number J, the points scattered and failed to show a regularity.) Hence this extrapolation yields a corrected value for $l\int\alpha_\nu d\nu$. The correction does not change the order of magnitude. It is negligible for weak lines, but for the strongest lines the observed intensity seems to be only a little more than 50 percent of the real intensity.

(b) Corrected results

The corrected values of $l\int\alpha d\nu$ are given in Table II, column III. From this value the concentrations of dispersion electrons given in column IV were deduced. The concentrations N_{rad} of OH radicals for the lower state of the absorption lines, computed from the OH pressure and the Boltzmann distribution (Section IIIb) are given in V. Finally, column VI gives the principal result, the f values $=N_{\text{el}}/N_{\text{rad}}$ for the various absorption lines for which column I gives the lower level.

The quantum theoretical expression for the probabilities of spontaneous transition are Einstein's a_{ki} values. Their relation to the f values, as discussed by Ladenburg,[19] is given by $a_{ki}=g_k/g_i\times(8\pi^2e^2\nu^2)/mc\times f$ (notation the same as in Section IIIa; ν in cm^{-1}; g_k and g_i=statistical weights of upper and lower levels, respectively). Column VII gives the a_{ki} values of the various lines.

The relation of our results to the recent results of Avramenko and Kondratjew,[20] although apparently contradictory, yet furnishing a good confirmation, will be discussed in a subsequent paper.

(c) Accuracy and sensitivity

(α) *Accuracy.*—Errors were due to the uncertainty of the equilibrium constant and to the imperfections of the spectrograph.

The *equilibrium constant* is uncertain largely because of the uncertainty in the energy of dis-

TABLE II. *f values.*

I	II	III	IV	V	VI	VII
Line	$l\int\alpha d\nu$ uncorrected (cm^{-1})	$l\int\alpha d\nu$ corrected (cm^{-1})	N_{el} $\times10^{-10}$ (cm^{-3})	N_{rad} $\times10^{-13}$ (cm^{-3})	$f\times10^4$	$a_{ki}\times10^{-5}$ (sec.$^{-1}$)
$Q_1(1\frac{1}{2})$	0.226	0.268	0.681	4.16	1.64	1.15
$(2\frac{1}{2})$	0.286	0.465	1.18	5.74	2.06	1.44
$(3\frac{1}{2})$	0.354	0.613	1.56	6.83	2.28	1.60
$(4\frac{1}{2})$	0.388	0.708	1.80	7.32	2.46	1.73
$(5\frac{1}{2})$	0.376	0.731	1.86	7.28	2.55	1.79
$(6\frac{1}{2})$	0.358	0.708	1.80	6.83	2.64	1.85
$R_2(\frac{1}{2})$	0.068	0.070	0.18	1.83	0.97	0.69
$(1\frac{1}{2})$	0.122	0.140	0.36	3.42	1.04	0.73
$(2\frac{1}{2})$	0.165	0.203	0.51	4.66	1.10	0.77
$P_1(1\frac{1}{2})$	0.218	0.280	0.71	4.16	1.71	1.20
$(2\frac{1}{2})$	0.272	0.348	0.88	5.74	1.54	1.08
$Q_{P_{21}}(1\frac{1}{2})$	0.136	0.187	0.47	4.16	1.14	0.80
$(2\frac{1}{2})$	0.152	0.168	0.43	5.74	0.74	0.52
$(3\frac{1}{2})$	0.120	0.130	0.33	6.83	0.48	0.34
$(4\frac{1}{2})$	0.094	0.101	0.26	7.32	0.35	0.24
$(5\frac{1}{2})$	0.053	0.077	0.20	7.28	0.27	0.19
$(6\frac{1}{2})$	0.036	0.056	0.14	6.83	0.21	0.15

[19] R. Ladenburg, Zeits. f. Physik **4**, 451 (1921). These a_{ki} values differ from the probability values, introduced by Füchtbauer (Physik. Zeits. **21**, 822 (1920)) and applied in the recent review of Margenau and Watson (Rev. Mod. Phys. **8**, 29 (1936)).

[20] L. Avramenko and V. Kondratjew, Acta physicochem. U. S. S. R. **7**, 567 (1937).

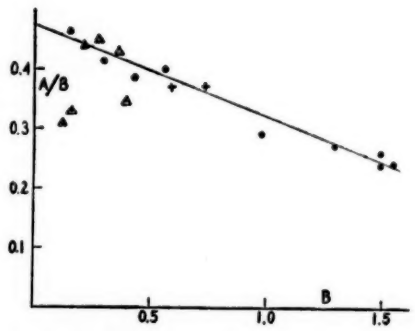

FIG. 4. Correction for lack of resolving power. A, observed values of $1\int\alpha_\nu d\nu$; B, Boltzmann factor × Hill and Van Vleck intensity factor; solid circle, Q_1; open circle, R_2; cross, P_1; triangle, ${}^QP_{21}$. (The two points farthest from the curve are derived from weak lines close to strong ones, and are accordingly of low weight.) Corrected values of $l\int\alpha_\nu d\nu = 0.475B$.

sociation $H_2O \rightarrow H+OH$. How large an effect this uncertainty has on the concentration of OH becomes evident from a table computed by Avramenko and Kondratjew.[20] A more accurate determination of this constant may necessitate a recomputation of N_{rad} of Table I, but not a repetition of the experiment. In the estimate of accuracy, we disregard this source of error; it is hardly possible to estimate the limit of this error; moreover we believe that the spectroscopic determination of the energy of dissociation may be improved so that this error may be eliminated in the future.

Scattered light in the spectrograph is negligible for large concave gratings, and is much fainter than that of plane gratings in a Littrow mounting in which reflection on the lens may be responsible for a considerable fog. In the concave grating even intense and rich emission spectra produce no appreciable diffuse light, presumably less than in any other instrument.

One might expect "ghosts," caused by imperfections of the grating, to affect the absorption lines because the ghost from the surrounding emission may raise the intensity at the bottom of the absorption line and so reduce the intensity of the observed absorption. That this is not the case in our spectrograph becomes evident from the following consideration. In the first place the Rowland grating used is known to have ghosts of negligible intensity, even in the neighborhood of over-exposed emission lines. Moreover, it can be shown that if a grating shows ghosts in *emission*, an absorption spectrum taken with the same grating must show ghosts as apparent *absorption* lines at the same distance and relative intensity. Actually the observed absorption spectra failed to show even the slightest traces of such ghosts. Their absence is evident on the densitometer trace (Fig. 2). As faint absorption lines may be lost on the densitometer record, it is more critical that no trace of a ghost can be seen on the absorption spectrum. It is concluded that the intensities of the absorption lines are not seriously obscured by a ghost background.

A source of error, the effect of which could be quantitatively estimated, was the lack of resolving power. There is no doubt that the resolving power of the grating approaches reasonably well the theoretical value. A possible effect of a deficiency was corrected in Section IVa. This correction leads to f values defined well within 15 percent. We do not believe that the error is much larger, since there is a great difficulty only in the investigation of *intense* absorption lines where a small change of the intensities observed at the bottom strongly affects $\int\alpha d\nu$. On the other hand, for absorption lines that are inherently *weak at the center* the resolving power of the spectrograph does not cause a *systematic* error, because it makes no difference whether or not the spectrograph shows the absorption spreading over too wide a range, provided that the intensity dip remains deep enough for measurement.

It seems impossible in the investigation of the OH bands to duplicate the high accuracy with which f values of a few outstanding *atomic* lines are known. This difficulty, however, does not make the investigation of the OH bands useless. Its chief aim is its application to reacting gases for the purpose of determining the probabilities of elementary reactions. For this end our accuracy, estimated at 15 percent, is sufficient, because in chemical investigations other major difficulties enter—such as possible wall reactions—which affect our spectroscopic investigation of the reaction as well as the chemical approaches to the same problem.

(β) *Sensitivity.*—The minimum concentration detectable is estimated as follows. The faint absorption line $R_2(\frac{1}{2})$ shows up quite well on the

densitometer trace. It is estimated that a line of $\frac{1}{3}$ this intensity would still be observed by direct scrutiny of the photographic plate, although it might be difficult to locate on the trace. This corresponds to an integrated absorption coefficient $l\int\alpha d\nu = 0.023$ cm^{-1}. The most intense line $Q_1(5\frac{1}{2})$ would show up with the same intensity for a partial pressure of OH = 0.01 mm. This applies to a furnace of 44 cm length.

In other experiments which were made with electric discharges through H_2O vapor[21] the absorbing layer was 150 cm long. Furthermore the temperature was nearly room temperature so that the rotational distribution was restricted to a smaller range. In a subsequent paper it will be shown that partial pressures of hydroxyl as low as 0.0008 mm are detectable with absorption spectra taken with the 21-foot grating.

It is evident that for other molecules for which the transitions observed are not half-forbidden, the absorption spectra may provide far more sensitive tests.

VI. Discussion

(a) Comparison with other f values

The f values of the principal absorption lines of *atoms* are of the order of magnitude of unity if the transition is not restricted by a selection rule; for example, 0.25 and 0.5 are the f values for the two D lines of Na. For the line 2537 of Hg, the f value is only 0.03, indicating a half-forbidden intercombination line.

In *molecular* spectra the f values are not diminished by the fact that a single line can be absorbed only by a small percentage of all molecules; this reduction is fully taken into account by the thermal distribution (Section IIIb(β)).

The only band spectrum for which the f value has been measured is closely related to the D lines of Na; it is the principal absorption band of the Li_2 molecule, $^1\Sigma \rightarrow {}^1\Sigma$, which in the limit of dissociation corresponds with the $^2P \rightarrow {}^2S$ transition of the Li atom.[22] For single lines of this spectrum Ladenburg and Levy found f values between 0.008 and 0.045. These small values are partly explained by the fact that in the molecule each initial state has more possible transitions than in the atom because of the simultaneous changes of rotation and vibration. In particular the changes of vibration may spread over a considerable range of quantum numbers as explained by the Franck-Condon rule.

For the visible I_2 bands Füchtbauer and Hofmann[23] reported an f value of the order of magnitude 10^{-6}. However, they compared the "number of dispersion electrons," derived from the intensity of the absorption spectrum, with the *total* number of I_2 molecules present, irrespective of the thermal distribution over vibration and rotation, as the analysis of band spectra was still unknown. The rotational energy distribution in I_2 near room temperature includes so many quanta that the individual quantum may have a probability of 1/100. But, in any case, an f value is obtained which is small as compared to unity.

The OH bands have f values much smaller than the Li_2 bands. This is explained—as Professor Van Vleck pointed out to us—by the property of the corresponding transition belonging to the pair of dissociated atoms. The dissociation products of the normal state are probably $O^3P + H^2S$, and of the excited state $O^1D + H^2S$.[24] The $^3P \rightarrow {}^1D$ transition of the O atom is forbidden and so explains the small probability of transition of the molecule. The high intensity by which the OH bands intrude as an impurity effect in discharge tubes does not point to high probability of transition but to the tendency of the H_2O molecule to cover all surfaces and come off gradually under the effect of the discharge.

(b) Lifetime of the excited state

The *lifetime* of the excited state is of interest for experiments in which *collisions during the lifetime* affect the observed spectrum. This lifetime is the reciprocal of the probability of transition expressed by Einstein's a_{ki} value, provided that there is only one transition possible, for example, for each of the D lines of Na. If several transitions can occur from the same

[21] To be published.
[22] R. Ladenburg and S. Levy, Zeits. f. Physik **88**, 449 (1934).
[23] C. Füchtbauer and W. Hofmann, Ann. d. Physik **43**, 127 (1914).
[24] H. Sponer, *Molekulspektren* (Julius Springer, 1935), p. 27.

excited level the lifetime is derived from the *total* probability of transition, that is, the sum of the a_{ki} values.

The computation of the lifetime, which is nearly the same for all initial levels of the same band, was carried through for the initial level of $Q_1(4\frac{1}{2})$. From the same level the fainter lines $R_1(3\frac{1}{2})$ and ${}^{Q}R_{12}$ $(4\frac{1}{2})$ originate (neglecting two very faint satellites). From the intensity formulae of the Hill-Van Vleck theory the relative intensities of these lines follow, respectively, as 2.10; 0.63; 0.24. The next change of *vibrational* quantum number which belongs to the 0→1 emission band is very improbable, as indicated by the relatively very small intensity of the 3428 band; hence all transitions from $v'=0$ to higher vibrations of the lower electronic level can be disregarded. In this respect the computation of the lifetime is much simpler for OH than for many other molecules. Furthermore, we assumed that there is no other *electronic* transition competing with the 3064 band since no other band system of the neutral hydroxyl is known.

The resulting lifetime is 3.8×10^{-6} sec. On the other hand the lifetime to be expected at the wave-length 3100A, computed from the radiation damping of the corresponding electromagnetic dipole, is 0.4×10^{-8} sec. The smaller value of the actual lifetime indicates a half-forbidden transition.

This long lifetime has a bearing on certain results on the persistence of rotation in collisions. In preceding papers abnormal rotation of OH as produced by the discharge and its persistence in collisions was discussed.[25] A few cm of He added hardly affected the observed abnormal rotation. In all the estimates a normal lifetime of the order of magnitude 10^{-8} sec. was assumed. On the basis of our present results the lifetime is much longer and therefore the chance for collisions during the lifetime much higher. Lyman and Jenkins,[26] in careful photometric work, found that the addition of 2 cm He to a discharge through H_2O caused only a minor reduction of the high rotation. With our value of the lifetime (applying the gas kinetic cross section of the water molecule to the excited OH radical), we computed that 570 collisions during the lifetime are rather inefficient in bringing about thermal equilibrium.

[25] O. Oldenberg, Phys. Rev. **46**, 210 (1934).
[26] E. R. Lyman and F. A. Jenkins, Phys. Rev. **53**, 214 (1938).

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The Absolute Rates of Heterogeneous Reactions

I. The General Theory of Adsorption*

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The statistical theory of reaction rates, developed by Eyring for homogeneous reactions, is extended to include heterogeneous reactions. It is shown that rates of adsorption and desorption are governed by the same form of mathematical expression in terms of partition functions of the system as rates of homogeneous reactions, provided only that for the activated state a "super-partition function," formed by adding together the partition functions for all the active spots, is used. The pseudothermodynamical form of the rate constant form is discussed, and illustrated by applications to special cases.

IT has been shown by Eyring[1] that the rate constant k_1 of a homogeneous chemical reaction may be represented by an expression of the form

$$k_1=\kappa\frac{kT}{h},\ \frac{Z^*}{\Pi_i Z_i}, \qquad (1)$$

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.
[1] Eyring, J. Chem. Phys. **3**, 107 (1935); Eyring and Wynne-Jones, J. Chem. Phys. **3**, 492 (1935).

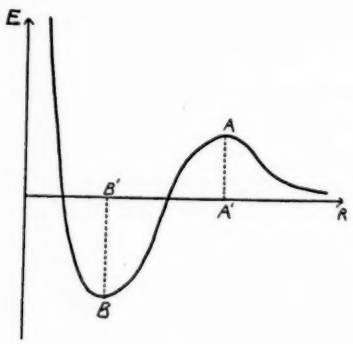

FIG. 1.

where k is Boltzmann's constant, T the absolute temperature, h is Planck's constant, and κ is the transmission coefficient, i.e. the fraction of the molecules reaching the critical configuration which react. $\Pi_i Z_i$ is the product of the partition functions of the reactants and Z^* is the partition function for the "pseudo-molecule" formed at the critical configuration.

We wish here to discuss the modifications which are necessary to extend the theory to include adsorption processes. The chief differences between the heterogeneous and the homogeneous cases are (1) the adsorbent surface will in general be composed of a large number of "active spots" at which adsorption may take place, and (2) adsorption will generally be limited to a unimolecular layer. The total number of active spots is not, however, usually equal to the total number of molecules which can be adsorbed by the surface. Instead, each active spot is a gateway, through which each molecule being adsorbed must pass, leading to a more or less extensive hinterland. Until this hinterland is completely filled, the active spot will remain active. We may, however, treat as special cases surfaces in which the active spots may hold either a single molecule or an infinite number.

A typical potential energy curve for a molecule in the adsorption process is shown in Fig. 1. In most cases there will be some activation energy to be overcome. This is represented by the hump with its top at A. The activation energy itself is given by AA'. The molecule finally reaches a point of equilibrium at B. The heat of adsorption is given by BB'. The point B is not necessarily the final position of the molecule: there may be other points on the surface with greater binding energies, separated from B by other activation passes. If these passes are higher than A, the rate of adsorption will be determined by the rate of passage over the secondary humps. For the present, however, we shall assume that the rate of adsorption is determined by the rate of passage over the hump A.

Neither the activation energy nor the heat of adsorption will be constant as we go from active spot to active spot. In fact it may be the case that these quantities depend not only on the active spot itself, but also on whether or not the neighboring spots are occupied. For the sake of simplicity, however, we shall assume that each spot is characterized by a definite activation energy and energy of adsorption. The active spots may then be divided into types, each type with its characteristic potential surface. In particular each type will have its own activation energy and heat of adsorption. We shall denote the number of active spots of the αth type which are not completely filled by $K^{(\alpha)}$. At the beginning of adsorption each $K^{(\alpha)}$ will be simply equal to the total number of active spots of the αth type, $K_0^{(\alpha)}$, but as adsorption goes on $K^{(\alpha)}$ will gradually decrease.

In order to make the definitions of "adsorbed" and "desorbed" molecule exact, we shall imagine the potential surface for each spot to be divided by two parallel planes at a small distance δ apart, at the summit of the activation hill, and perpendicular to the direction of motion of a molecule following the path of least resistance. Any molecule which is in the region between the inner plane and the surface we shall call an adsorbed molecule: any molecule between the planes, an activated molecule; and any molecule outside the planes, a desorbed molecule.

The molecules of the system can then be divided into groups: (1) the molecules adsorbed on an active spot of the αth type, (2) molecules activated at an active spot of the αth type, (3) desorbed molecules. For each of these groups of molecules there can be set up a partition function. We shall denote the partition functions for these three groups by $Z_a^{(\alpha)}$, $Z_0^{(\alpha)}$, and Z_d. We shall also let $N_a^{(\alpha)}$, $N_0^{(\alpha)}$, and N_d be the numbers of molecules in the three groups.

By an obvious generalization of a well-known theorem of statistical mechanics[2] the values of $N_a^{(\alpha)}$, $N_0^{(\alpha)}$, and N_d when the whole system is at equilibrium are given by

$$N_d : N_a^{(\alpha)} : N_0^{(\alpha)} = Z_d : K^{(\alpha)}Z_a^{(\alpha)} : K^{(\alpha)}Z_0^{(\alpha)}. \quad (2)$$

This gives immediately

$$N_0^{(\alpha)} = N_d K^{(\alpha)} Z_0^{(\alpha)} / Z_d \quad (3)$$

for the number of activated molecules.

Following Eyring[1] we shall assume that during the actual adsorption process the desorbed molecules remain essentially in statistical equilibrium. We also assume that the activated molecules moving toward the surface are also in equilibrium with the desorbed molecules. Eyring's argument then gives immediately for the rate of adsorption on the spots of the αth type

$$\kappa \frac{kT}{h} N_d \frac{K^{(\alpha)} Z_*^{(\alpha)}}{Z_d}, \quad (4)$$

where we have now put

$$Z_0^{(\alpha)} = \frac{(2\pi mkT)^{\frac{1}{2}}}{h} \delta Z_*^{(\alpha)}, \quad (5)$$

$Z_*^{(\alpha)}$ being the partition function for a molecule "frozen" in place at the top of the potential barrier.

The total rate of adsorption on the whole surface is then

$$\kappa \frac{kT}{h} \frac{N_d}{Z_d} \Sigma_\alpha K^{(\alpha)} Z^{*(\alpha)}. \quad (6)$$

Remembering that any partition function is of the form $\Sigma_i e^{-E_i/kT}$, where the sum is over all possible energy levels, and E_i is the energy of the ith level, we see that the expression $\Sigma_\alpha K^{(\alpha)} Z_*^{(\alpha)}$ in (6) is of the same nature as a single partition function. It consists of a sum of terms of the form $e^{-E_i/kT}$, but in it every energy level for every active spot is included, even exact duplicates being counted as many times as they appear. If we denote this "super-partition function" $\Sigma_\alpha K^{(\alpha)} Z_*^{(\alpha)}$ by Z^*, (6) becomes

$$\kappa \frac{kT}{h} \frac{N_d}{Z_d} Z^* \quad (7)$$

and the rate constant for the adsorption, k_a, becomes

$$k_a = \kappa \frac{kT}{h} \frac{Z^*}{Z_d}. \quad (8)$$

Formally, this equation is exactly the same as (1), but it must be remembered that in (1) Z^* represents the partition function for a *single* type of activated molecule, while in (8) Z^* is the *sum* of the partition functions for the activated points of all the active spots.

It is interesting to note that (7) reduces to the "classical" expression for the number of collisions with a surface if the appropriate assumptions are made. These are (1) that the surface is a plane surface of area S, (2) that the molecules may be treated as mass points, and (3) every collision is effective, i.e., there is no activation energy of adsorption and $\kappa = 1$. If we introduce these assumptions into our theory we find

$$Z_d = \frac{(2\pi mkT)^{\frac{1}{2}}}{h^3} V,$$

while Z^* reduces to the partition function for a two-dimensional gas

$$Z^* = \frac{2\pi mkTS}{h^2}.$$

Hence the rate of collision is, by (7)

$$\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{N_d S}{V}, \quad (9)$$

which is identical with the classical expression.

Instead of using the partition functions, it is sometimes convenient to use instead the more usual thermodynamic functions of the system. For systems at equilibrium the relation between these is

$$Z = Ne^{-F/RT}, \quad (10)$$

where Z is the partition function for the system, N is the number of molecules in the system, and

[2] Cf. Fowler, *Statistical Mechanics*, second edition (Cambridge, 1937), p. 160.

F is the chemical potential (partial molal free energy). It must be born in mind that the dependence of the right side of (10) on N is only apparent, for Z is independent of the number of molecules. Because of this fact, it is not necessary to use the value of F for the actual state of the system, and it is equally valid to use the value of F in any arbitrarily chosen standard state at the same temperature, provided that the number of molecules, N, be taken to be the number in the standard state. Neglect of this fact has led to needless controversy in the past.

We may formally use (10) for the partition function Z^* as well as Z_d. The corresponding chemical potential F^* will then not be a true thermodynamic quantity, but behaves mathematically in exactly the same way as a chemical potential.

In terms of F_d, the chemical potential of the desorbed molecules, and F^*, Eq. (8) becomes

$$k_a = \kappa \frac{kT}{h} \frac{N^*}{N_d} e^{-(F^*-F_d)/RT}. \qquad (11)$$

If we choose an arbitrary standard state for the desorbed and activated states, and moreover choose them in such a way that $N^* = N_d$, then

$$k_a = \kappa(kT/h)e^{-\Delta F^*/RT}, \qquad (12)$$

where $\Delta F^* = F^* - F_d$. Separation of ΔF^* into an entropy and heat content of activation by

$$\Delta F^* = \Delta H^* - T\Delta S^*$$

then gives

$$k_a = \kappa(kT/h)e^{\Delta S^*/R}e^{-\Delta H^*/RT}. \qquad (13)$$

Before this theory can be applied, it is necessary to obtain some idea as to the values to be expected for ΔS^* and ΔH^*. For gases, the standard state usually chosen is that in which the pressure is one atmosphere. The number of molecules in the standard state is then $N_d = P_0V/kT$, where $P_0 = 1.013 \times 10^6$ dynes/cm^2. In order to use Eqs. (12) and (13) it is therefore necessary to choose as the standard state for the activated molecule one in which the same number, P_0V/kT of molecules are in the activated state: i.e. the pseudothermodynamic functions for the activated state will depend on the volume of the gas phase! This results in rather "queer" values of the entropy of the activated molecules, as will be seen presently.

For the purposes of rough estimates, the motion of a molecule may be considered in terms of translations, rotations, and vibrations. Each degree of translational freedom is characterized by a mass, m; each rotation by a moment of inertia, I, if two dimensional, or three moments, A, B, and C, if three dimensional; each vibration by a frequency, ν, or a characteristic temperature $\Theta = h\nu/k$. The contributions of each of these motions, the "zero-point energy" (which includes the energy of activation), and the terms arising from the choice of standard state through the factor N in (10) to H and S are well known and are shown in Table I. The typical values given are for a temperature of 300°K, a mass of one atomic weight unit, a moment of inertia of 10^{-40} g cm^2 and a characteristic temperature Θ of 500°K.

An examination of the numerical values of H and S shows the following important facts: the zero-point energy contributes nothing to S, but appears *in toto* in H. The remaining terms in H are of the order of a few times RT. The value of H is therefore chiefly determined by the value of E_0, provided E_0 is not too small. On the other hand, the entropy is very sensitive to quantum effects. Thus we see that vibrations will even at fairly high temperatures contribute little to the entropy. The rotations contribute an appreciable amount, but much less than the translations.

The "standard state" correction will always cancel out when the difference between two entropies is taken, unless the total number of particles changes, when it becomes an important part of the entropy change. Because of the large negative value of this term for the usual standard state for gases, the entropies calculated for the adsorbed molecules come out with large negative values. This seeming contradiction to the concept of positive entropies is, however, only apparent, for the "standard state" we are forced to use is one which would be impossible to realize. (The entropy of a perfect gas could theoretically be made negative by a sufficient increase of pressure, because of the term $-R \ln P$. The necessary value of P is, however, about 10^5 atmospheres.)

Considering now the adsorbed (or activated)

molecules, there are two cases of great importance as simplified models. The first is that in which we may consider the adsorbed molecules as a two-dimensional gas. Omitting the terms due to the internal motions of the molecules, the entropy of such a two-dimensional gas is seen from Table I to have the form

$$S = R \ln \frac{2\pi m(kTe)^2 A}{h^2 P_0 V}, \tag{14}$$

where A is the area of the surface. The corresponding form for the three-dimensional desorbed gas is

$$S = R \ln \frac{(2\pi m)^{3/2}(kTe)^{5/2}}{h^3 P_0}. \tag{15}$$

The entropy of either adsorption or activation in this case is then

$$\Delta S^* = R \ln \frac{hA}{(2\pi mkTe)^{\frac{1}{2}} V}, \tag{16}$$

which is, then, the entropy of activation for the "classical" collision picture. It should be noticed, however, that for any molecules except those consisting of a single atom, there will also be an "internal" entropy of activation. In particular the rotation of the free molecules will be reduced to either two-dimensional rotations, or to vibrations. This will lead to a marked decrease in entropy for such molecules, i.e. to a greatly reduced rate of adsorption.

The other case is that in which the adsorbed molecules are firmly bound to the surface, so that the motion is purely vibrational. As a very highly idealized example, let us consider a model in which the molecules are adsorbed in such a fashion that the energy quantum of each vibration is so high that practically all the adsorbed molecules are in their lowest states, and that even at the top of the potential barrier the only possible motion is one translational degree of freedom. We shall refer to this as the case of "tight" adsorption. In this case the partition function Z^* is simply K_0, the total number of active spots which are empty. The entropy of the activated molecules is then

$$S^* = R \ln \frac{K_0 ekT}{P_0 V}. \tag{17}$$

Now an upper limit to K_0 is 10^{16} spots per square centimeter. At 300°K, S^* (referred to the usual standard state) is *less* than -13 cal./degree. Comparing this with the "classical" value of S^*, which is -12.7 cal./degree, we see that there is no sharp boundary between the two cases. In fact, the case of "tight" adsorption can be treated essentially as a "classical" adsorption if an area of about 10^{-16} cm^2 is assigned to each active spot.

TABLE I. *Table of contributions to the partial molal heat content and partial molal entropy. The translational contribution is per unit length. The vibrational contribution is the limiting form for low temperatures. The typical values are for the constants given in the text.*

Type of Motion	Contribution to		Typical Values	
	H	S	H	S
Zero-point energy	E_0	0		0
Translation (1 dimension)	$1/2\ RT$	$R \ln \frac{(2\pi mkTe)^{\frac{1}{2}}}{h}$	300	37.6
Rotation (2 dimensions)	RT	$R \ln \frac{8\pi^2 IkTe}{h^2}$	600	6.0
(3 dimensions)	$3/2\ RT$	$R \ln \frac{8\pi^2(8\pi^3 ABC)^{\frac{1}{2}}(kTe)^{\frac{3}{2}}}{h^3}$	900	10.1
Vibration	$R\Theta e^{-\Theta/T}$	$R(1+\Theta/T)e^{-\Theta/T}$	190	0.4
Standard State	RT	$R \ln \frac{kTe}{PV}$	600	-87.9

There is, however, one important difference between these cases. This arises from the saturation effects which may be expected from the case of "tight" adsorption. If each active spot can hold only one molecule, then we must expect to find the value of K_0 decreasing as adsorption goes on. Beside this direct effect on the reaction rate, another secondary effect may enter if the active spots show a wide range of values for their free energies of activation, for then the first adsorption will take place on those spots which show the smallest free energies of activation. The reaction velocity in these cases will show a very marked decrease with time.

As an example, let us consider the data of Burwell and Taylor[3] on the adsorption of H_2 on chromic oxide gel. Burwell and Taylor measured the rates of adsorption of H_2 (maintained at constant pressure) on this catalyst over the temperature range 195°K−491°K. The mechanism of the adsorption is evidently complex, for there is at each temperature a very rapid initial adsorption, followed by a slower adsorption. It was found, however, that if the initial adsorption is subtracted from the data at each temperature, the resulting time-adsorption curves are all similar. In fact if a "reduced" time t', defined by

$$t' = te^{-21,700/RT} \tag{18}$$

is substituted for the actual time, t, the "corrected" adsorption curves are identical. Burwell and Taylor did not attempt to analyse this curve further. I have made an exponential analysis of these data, and have found that all of them can be represented very closely by the equation

$$y = y_0 + 1.8(1-e^{-k_1 t'}) + 13.8(1-e^{-k_2 t'}) + 39.0(1-e^{-k_3 t'}), \tag{19}$$

in which y is the total amount adsorbed (cc of H_2 at *STP*) and y_0 is the initial adsorption, the rate of which is too fast to measure. The constants k_1, k_2, and k_3 have the values 1.08×10^{10}, 6.36×10^{8}, and 9.88×10^{7} min.$^{-1}$, respectively.

The form of Eq. (19) makes it clear that even the slow adsorption is not a simple process. An equation of this type can be obtained from a number of mechanisms, of which the simplest to assume would be one in which adsorption was taking place simultaneously at four different varieties of active spots. It is well known that if the rate of adsorption at one of the kinds of active spot were k' and the rate of desorption k'', the total amount adsorbed in time t would be

$$k'/k''(1-e^{-k''t}).$$

We can therefore regard (19) as the sum of four such expressions, the first having a very large value of k''. It is thus a simple matter to find the other three pairs of values of k' and k''. Expressing these in terms of the corresponding heats and entropies of activation, we obtain the result shown in Table II. The value 21,700 for the ΔH^* of all the processes involved is an immediate consequence of the fact that the time enters Eq. (19) only through t'.

Another, and equally good mechanism is one in which adsorption is followed by a series of consecutive, reversible reactions on the surface, e.g. a process in which the adsorbed molecules move away from the active spots to other unoccupied parts of the surface. While it is impossible to give any simple relation between the rate constants for these reactions the final form of the integrated rate expression is again of the same form as Eq. (19). It must be noted, however, that in this case too the values of ΔH^* for all the reactions involved must again be 21,700 cal., for the same argument which led to this result in the previous case still applies.

While other mechanisms are possible, these two seem the most plausible, and we shall confine our discussion to these. Considering the first of these mechanisms in the light of the present theory, two facts stand out at once. The first is that the value of ΔH^* is the same for all processes. This would be an extraordinary coincidence if the four adsorption processes were all independent, as this mechanism assumes. Moreover it implies a vanishing heat of adsorption, which is contrary to experience. Secondly, the values of ΔS^* in Table II are not those we have been led to expect for adsorption processes, but much larger. We are therefore forced to regard the first mechanism as highly improbable.

The second mechanism meets with less difficulty. In this case the true adsorption rate is the

[3] Burwell and Taylor, J. Am. Chem. Soc. **58**, 697 (1936).

TABLE II.

	ADSORPTION		DESORPTION	
	ΔH^*	ΔS^*	ΔH^*	ΔS^*
k_1	21,700	−20	21,700	−21
k_2	21,700	−22	21,700	−27
k_3	21,700	−24	21,700	−31

rate of the initial adsorption. It is unfortunate that the data do not permit an evaluation of this rate. The other rates involved are the rates of migration of the molecules (or possibly atoms) of hydrogen over the surface. It is still somewhat remarkable that the heats of activation are equal for all the processes involved, but such a situation is by no means inconceivable. That the heat of the reactions should vanish is not surprising, for the migration might very well lead to a new position of the same energy as that of a molecule adsorbed on an active spot.

The most plausible explanation of the data would then seem to be a process taking place in a series of steps. The first step is the adsorption proper on the active spots of the catalyst. The energy of activation of this process is probably much lower than the 21,700 characteristic of the later steps. This is followed by a process of migration, or "hopping" over the surface away from the active spots. There would seem to be at least three varieties of potential passes through which this process can take place, all with nearly the same height (21,700 cal.) but differing from each other in shape, so that the entropies of activation at the different passes are different, thus leading to different absolute rates for the various reactions.

TABLE III.

t°C	k CC/MIN.	k_{cor} CC/CM² SEC.	ΔF^*	ΔS^*	ΔH^*
0	3.72	2.70×10^{-3}	19,200	−55.0	4,100
15	5.87	4.25	20,000	−55.8	3,900
25	7.62	5.52	20,500	−56.3	3,800
35	9.55	6.92	21,100	−56.9	3,600
45	11.81	8.56	21,700	−57.4	3,400
55	14.26	10.33	22,300	−58.0	3,200
65	16.93	12.27	22,800	−58.5	3,100

As a second example, this time of adsorption from solution, let us consider the data of Van Name[4] on the reaction between cadmium metal surfaces and I_2 (or I_3^-). The rate constants given by Van Name are reproduced in Table III, together with the free energies, heats, and entropies of activation calculated from them. The rate constants are given first in Van Name's units, and then in the column k_{cor} when reduced to unit area and to sec.$^{-1}$. It will be noticed that in this case the entropies of activation are in good agreement with the values we should expect from the results of this paper. From the values of ΔH^* it is impossible to say whether or not the rate governing step is or is not diffusion to the surface. This is certainly just about the value we should expect for such a process, and the entropy of a diffusion process would not be appreciably different from that of an adsorption.

[4] Van Name, Am. J. Sci. **43**, 453 (1917).

Interpretation of the Properties of Zinc Sulphide Phosphors

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The properties of pure and copper activated zinc sulfide phosphors are described, and an attempt is made to interpret these properties following the plan of a previous paper on alkali halide phosphors activated by thallium. It is pointed out, as has been done by previous workers, that the combination of photoconductivity and bimolecular decay law of phosphorescence implies that an ionization process accompanies the excitation of zinc sulfide phosphors. By applying the ideas of the quantum theory of solids, it is shown that this ionization process does not correspond to the freeing of an electron from the Zn^{++} or S^{--} ions of the lattice. It is concluded that the pure ZnS phosphor probably contains neutral interstitial zinc atoms, and that these are responsible for the luminescence and photoconductivity. By analogous reasoning, it is concluded that the copper activated phosphor contains interstitial copper atoms. The relative stability of interstitial copper atoms and substitutional copper ions is discussed in terms of the Schottky-Wagner theory of deviations from stochiometrical proportions. It is concluded that the interstitial copper atoms probably are in a metastable condition.

1. INTRODUCTION

IN a previous paper[1] on the luminescence of crystals the properties of akali halides activated by thallium were discussed and interpreted in a tentative manner. It was found possible to relate the absorption and fluorescent spectra of these materials to the presence of monovalent thallium ions which are present in the lattice, substitutionally, replacing alkali metal ions. The weak phosphorescence which decays according to the laws of a monomolecular reaction was related to the properties of the small percentage of thallium ions which have other thallium ions as neighbors. In other words, these simple phosphors behave as though they consisted of a gas of monatomic thallium ions which contains a small percentage of diatomic thallium molecule ions. The fluorescent light is produced by an excitation process which is analogous to resonance excitation of the thallium ions. The phosphorescent light is produced by excitation of one of the thallium ions in a diatomic pair to a state above the resonance level. The valence electrons of the thallium ions should remain attached to the ion during all of these excitation processes, if the picture which is advanced is correct. Hence these phosphors should not become photo-conducting during excitation of phosphorescence. This seems to be in complete accordance with experimental work.

In the present paper the properties of zinc sulfide phosphors shall be discussed from a viewpoint similar to that used in the preceding paper. The experimental work relating to zinc sulfide, unlike that for the alkali halide phosphors,[1] is not summarized in any single series of papers. Many different investigators have contributed to present-day knowledge of these substances. We shall present a brief survey of the experimental conclusions in the next section, emphasizing only those experiments which are felt to be important for the present interpretation. This presentation will be followed by a tentative interpretation of the experimental work.

2. EXPERIMENTAL SURVEY OF THE LUMINESCENCE OF ZnS

Zinc sulfide exists in two crystallographic forms.[2] The low temperature form is known a zincblende or sphalerite and has a cubic lattice which is related to the structure of diamond. This form is obtained in ordinary precipitation methods of preparing zinc sulfide. The high temperature form, wurtzite, possesses a hexagonal structure in which the coordination number is four, just as in the cubic phase. The thermodynamical transition temperature for the phase change is not accurately known, but it is probably in the neighborhood of 400 or 500C. The transi-

[1] J. Chem. Phys. **6**, 150 (1938).

[2] *Structurberichte.*

tion proceeds very slowly at 660°C[3] and very rapidly at 900C. The hexagonal form does not revert to the cubic form at a measurable rate at room temperature unless the material is ground or is placed under high nonhydrostatic pressure.[4]

We shall proceed upon the assumption that the ordinary luminescent varieties of ZnS have the high temperature hexagonal structure. All of the ZnS phosphors are produced by heat treatment at temperatures above the thermodynamical transition point and an at least partial transition to the hexagonal phase takes place. Cubic ZnS phosphors have been reported in the literature,[5] but these materials were always a mixture of the two forms. It is the writer's opinion that the hexagonal form is responsible for the ordinary luminescence. It is conceivable that the cubic form could also be luminescent, but it seems unlikely that the type of changes which are needed in order to activate a crystal of ZnS can be brought about without causing the phase change as well. Theoretical reasons for this viewpoint will be discussed below.

A. Types of phosphors

We shall discuss the following two types of phosphors:

a. Pure ZnS. Pure zinc sulfide may be made[6] active by appropriate heat treatment. A typical procedure is to heat the material at 900°C for one-half hour. The color of the luminescence of the pure salt is light blue, and it may be excited by any radiation in the near ultraviolet.

b. Copper-activated ZnS.[7] This is the oldest and most commonly known variety of luminescent zinc sulfide. The luminescent light is brilliant green and is excited by radiation in the blue and near ultraviolet. The peak of this excitation band lies at a longer wave-length than the peak for the excitation of pure ZnS. The fraction of copper which is required to activate this luminescence is about 10^{-5}.

Zinc sulfide may be activated by introducing many foreign atoms other than copper. Examples of such substances are silver and manganese. We shall not deal explicitly with these cases because the experimental facts relating to them are not sufficient to furnish a complete picture. It is highly probable that the type of explanation which we shall develop in order to explain the foregoing two cases will apply *in toto* to a large number of these other cases.

B. Characteristic absorption of ZnS

Qualitative experiments carried on in this laboratory show that the peaks of the characteristic absorption bands of ZnS lie well below 2500A. This was proved by studying the transmission of films of zinc sulfide several microns thick which were evaporated on quartz. The tails of these peaks extend into the near ultraviolet. Since the relatively small peaks of the bands which stimulate luminescence lie entirely in the near ultraviolet, it is natural to assume that they arise from a process which is different from that of the fundamental peaks. This fact, which is similar to the facts for alkali halide phosphors, was appreciated by Lenard[8] very early in the study of zinc sulfide phosphors. To explain it, he assumed that a small number of irregularly placed atoms rather than the typical atoms of the bulk material are responsible for luminescence. In lieu of exact knowledge of the electronic structure of these active regions he referred to them as centers. We shall use this word in the same sense, accepting Lenard's viewpoint that the two peaks have different origin. Just as in the case of the alkali halide phosphors, a part of the object of this paper is to provide an interpretation of the structure of the center in the two cases which were discussed in A.

C. Decay characteristics of phosphorescence

Experimental measurements of the decay characteristics of zinc sulfide activated by copper seem to indicate that the emitted light is entirely phosphorescent[9] at room temperature. We have checked this in some cases at liquid-air temperatures by showing that the intensity of emitted light is zero when a specimen is first exposed to

[3] Experiments by Dr. N. T. Gordon and this laboratory.
[4] Guntz, Ann. d. Chemie **5**, 157 (1926) et seq. Lenard, *Handbuch der Experimental Physik*, Vol. 23, p. 267.
[5] Tiede and Schleede, Chem. Ber. **53**, 1721 (1920).
[6] Schleede, Zeits. f. angew. Chemie **48**, 277 (1935). Riehl, Ann. d. Physik **29**, 636 (1937).
[7] Discovered by Sidot, Comptes rendus **63**, 188 (1866).
[8] Lenard and Tomaschek, *Handbuch der Experimental Physik*, Vol. 13 (1928), pp. 1 and 2.
[9] Perkins and Kaufmann, Pub. No. ST38, R.C.A. Res. and Dev. Lab. Riehl and Ortmann, Ann. d. Physik **29**, 556 (1937).

3650A radiation. The emission becomes appreciable only after several seconds of exposure.

The decay of intensity in copper activated material is given[10] fairly closely by the equation

$$(I(0)/I(t))^{\frac{1}{2}}=\alpha t+1, \tag{1}$$

where $I(t)$ is the intensity at time t and α is a constant which is temperature dependent, decreasing with decreasing temperature. This decay law implies that the number of excited centers which are left after time t if there are N_0 at time $t=0$ is given approximately by the equation

$$N=N_0/(\alpha t+1). \tag{2}$$

Deviations from (1) are observed at small values of t.

Equation (2) is characteristic of a bimolecular reaction, that is, of a reaction in which two perfect gases A and B combine to form AB. This type of decay law is to be distinguished from the exponential type observed in the alkali halide phosphors.

The decay characteristics of pure zinc sulfide phosphors have not been measured quantitatively, but they show the same temperature-dependent characteristics as the copper activated phosphors. We shall assume that the law (1) is valid in this case too.

D. Photoconductivity

The photoconductivity of zinc sulfide activated by copper was investigated by Gudden and Pohl[11] in 1920. They found that the absorption peaks for stimulating luminescence and photoconductivity are practically identical. The pure sulfide phosphor does not seem to have been[12] investigated for photoconductivity, but it should be photoconducting if our assumption that there is a one-to-one correspondence between the properties of the two types is correct.

[10] Antonow-Romanowsky, Physik. Zeits. Sowjetunion **7**, 366 (1935).

[11] Cf. Gudden, *Photoelectric Phenomena* (Springer, 1928).

[12] Gudden and Pohl [Zeits. f. Physik **2**, 181 (1920)] report finding photoconductivity in "impurity free" zinc sulfide. They do not describe the luminescent properties of this material. Incidentally they report conductivity in the manganese activated phosphor.

3. Interpretation of the Properties of the Phosphors

The key to the interpretation of the zinc sulfide phosphors evidently is the coexistence of photoconductivity and phosphorescence with the bimolecular decay law. These facts indicate that the absorption process results in ionization of the center and that the phosphorescence is a consequence of the subsequent recombination of the electrons with the ionized centers. This view has been expressed in a number of papers[13] and will not be amplified further in this one. The fundamental problem is: What is ionized during the absorption of light? We shall attempt to answer this question first for the pure sulfide phosphor and then for the copper activated substance. Before doing this, however, we shall discuss the probable origin of the fundamental peaks in pure zinc sulfide.

A. The fundamental absorption bands of zinc sulfide

The Madelung potential at a negative ion in the wurtzite lattice is[14]

$$V_M=1.64(Ze/r), \tag{3}$$

where Z is the valence of the positive ions and r is the distance between nearest unlike ions. The value of V_M for positive ions is the negative of this. Using this and data concerning the ions Zn^{++} and S^{--} we may determine the relative energy of electrons in the lattice.

The electron affinity of S^{--} as determined from the Born cycle is about -90 kcal. or about -4 ev. Lozier[15] has found that this characteristic instability of divalent negative ions is due entirely to the second electron in the case of O^{--}. The affinity of the first electron is 2.2 ± 0.2 ev. Since the affinities of the halogens decrease with increasing atomic number, we shall assume that the affinity for the first electron in sulfur is less than that for oxygen and shall select a value of 1 ev. The affinity for the second is then about -5 ev. The energy of S^{--} relative to that of S^- is shown on the right-hand side of Fig. 1 as

[13] Cf. reference 11. Also Blochinzew, Physik. Zeits. Sowjetunion 586 (1937), and Reimann, Nature **140**, 501 (1937).

[14] Hund, Zeits. f. Physik **34**, 833 (1925). Gross, Zeits. f. Krist. **76**, 565 (1931).

[15] Lozier, Phys. Rev. **46**, 268 (1934).

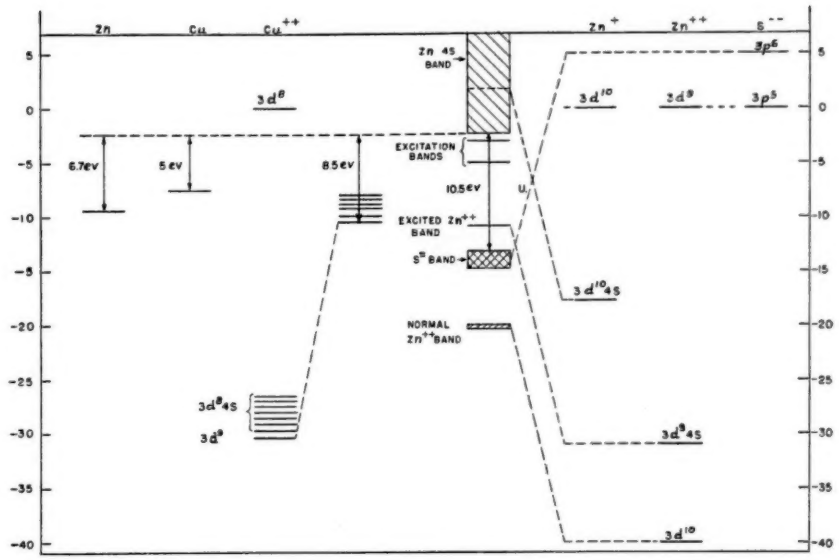

FIG. 1. Behavior of atomic and ionic energy levels before and after formation of zinc sulfide lattice.

the position of a $3p^6$ configuration relative to a $3p^5$.

The energy of the various states of Zn^{++} relative to the ground state of Zn^{+++} (d^9 configuration) is shown in the second column from the right in Fig. 1. The energy required to ionize Zn^{++} is 40 ev. Hence the normal state of Zn^{++} is placed at -40 ev in this diagram. The first excited state of Zn^{++} (corresponding to $3d^9 4s$) is about 9 ev relative to the lowest state.

The lowest state of Zn^{+} relative to $3d^{10}$ is given in the third column from the right in Fig. 1. We shall use this in estimating the energy required to transfer an electron from the sulfur ion to the zinc ion.

The dotted lines in Fig. 1 show the way in which the electronic energy changes as ions are brought together to form the wurtzite lattice. The energy of electrons on negative ions is decreased by an amount (3), Z being 2 in the present case. The energy of electrons on positive ions is increased by the same amount. In addition to this displacement, the levels broaden into bands in accordance with the band theory of solids. We can estimate the broadening only roughly. By analogy with the negative ion band[16] in the alkali halides we may expect the S^{--} level to broaden by several ev. The broadening of the $4s$ level of Zn^{+} can be estimated roughly from the broadening of the $4s$ level in metallic copper which was investigated by Fuchs,[17] since the broadening is determined mainly by the interatomic distance. In this way the writer has decided that the lower edge of the $4s$ band is about 4 ev below the energy determined by adding the Madelung energy to the $3d^{10}4s$ level of atomic zinc. The relative positions of the various bands and levels in zinc sulfide are shown in the fourth column from the right of Fig. 1. The highest band is the $4s$ band and about 10.5 ev below it is the p^6 band of the sulfur ion electrons. Below this is the band of the outer electrons of Zn^{++}. The line 9 ev above this is the first excited level of the Zn^{++} ion. It is assumed that this excitation energy does not change appreciably in going from the free ion to the solid. The lines immediately under the $4s$ band correspond to the excitation bands of the sulfur ion. In the atomic picture of solids these levels correspond to transfer of electrons from the S^{--} ions to the nearest neighboring Zn^{++} in a way such as that described in reference 1. We have computed roughly the position of these levels in the manner employed by von Hippel,[18] which is

[16] Shockley, Phys. Rev. **50**, 754 (1936). Ewing and Seitz, Phys. Rev. **50**, 760 (1936).

[17] Fuchs, Proc. Roy. Soc. **151**, 585 (1935).

[18] von Hippel, Zeits. f. Physik **101**, 680 (1936).

based on an earlier method of Gudden and Pohl. The lowest of these excitation levels which is analogous to a p^5S state of S^{--} turns out to be about 7 ev above the S^{--} p^6 band. This should be the first excited state of the ideal crystal of zinc sulfide if the rough computational methods employed here are approximately correct. The transition to the 4*s* or conduction band requires about 11 ev. Hence the excitation bands should lie between about 1800A and 1100A, according to this picture. Since the first excited state of Zn^{++} is 9 ev above the d^{10} ground state, we may expect that the bands corresponding to excitation of Zn^{++} and of S^{--} will overlap.

Let us suppose that some Zn^{++} ions are replaced by Cu^{++} ions. The position of the normal state of Cu^{++} relative to that of Cu^{+++} ($3d^8$) is shown in the third column from the left of Fig. 1.[19] As cupric ions are brought into the lattice in Zn^{++} positions, the energy of a valence electron on the Cu^{++} ion is raised to the positions shown in the fourth column from the left in Fig. 1. The ground level of the ion is roughly 8 ev below the conduction band of the solid, implying that photoconductivity would be observed only in the far ultraviolet if copper ions could enter the zinc sulfide lattice only substitutionally, replacing Zn^{++} ions. Incidentally, it should be observed that the color of pure cupric salts may be ascribed to the closeness of the $3d^9$ and $3d^84s$ configurations.

To summarize, we may say that the observed positions of the fundamental absorption peaks of zinc sulfide can be explained semiquantitatively in terms of simple energy-level diagrams of the type used in alkali halide lattices. There is no reason for expecting photoconductivity for near ultraviolet quanta in the ideal zinc sulfide lattice or in a zinc sulfide lattice in which some of the zinc ions are replaced by cupric ions.

B. Luminescence of pure zinc sulfide

A clue concerning the nature of pure luminescent zinc sulfide is provided by the investigations of Wagner,[20] Baumbach, Fritsch and their co-workers on the electron conductivity of zinc oxide. This oxide has the same crystal structure as the luminescent form of zinc sulfide. Experiments of the same type carried out on zinc sulfide would obviously be preferable for our purposes, but it seems safe to assume that the two materials have analagous properties. As a matter of fact, experiments carried on in this laboratory indicate that zinc oxide has luminescent properties which are qualitatively identical with these of zinc sulfide.

Zinc oxide is a typical semiconductor. Specimens which have been heated in a vacuum for a considerable length of time exhibit at room temperature an appreciable electronic conductivity which decreases with decreasing temperature. At room temperature and at lower temperatures the temperature dependence is described approximately by the equation

$$\sigma = Ae^{-\epsilon/kT}, \tag{4}$$

where σ is the conductivity, A is practically constant, and ϵ is a constant which varies between 1 and 0.01 ev, depending upon the specimen and type of heat treatment it has received. In general, ϵ is smaller the longer the specimen has been heated in a vacuum.

Hall effect and thermoelectric measurements show that this conductivity is principally electronic and that the carriers are negative charges; that is, the sign of the Hall coefficient is the same as in bismuth. In addition, there is a very small positive ion transport number. This indicates that the zinc ions are considerably more mobile than are the oxygen ions.

The conductivity of conducting zinc oxide is dependent upon the vapor pressure of oxygen with which a specimen is at equilibrium during its high temperature heat treatment. Generally speaking, the higher the vapor pressure of oxygen the lower is the room temperature conductivity. The room temperature conductivity of some specimens has been reduced by as much as one million by heating at 1000°C in one hundred atmospheres of oxygen for several days. Large changes of this type are usually due to changes in both A and ϵ in (4). The first constant decreases and the second increases with oxygen pressure. The dependence of A on oxygen pressure, p_{O_2}, is

[19] I am indebted to Professor A. G. Shenstone for the estimate of the ionization energy of Cu^{++} which is used in this diagram.

[20] Wagner, Zeits. f. physik. Chemie **B22**, 181 (1933) et seq. Wagner and Baumbach, Zeits. f. physik. Chemie **22**, 199 (1933). Fritsch, Ann. d. Physik **22**, 375 (1935).

described roughly by the equation

$$A = C p_{O_2}^{1/4.3}, \tag{5}$$

where C is a constant.

From this dependence of A and the sign of the Hall effect, Wagner[20] concludes that the composition of conducting zinc oxide deviates from strict stoichiometric proportions and that there is an excess of zinc. One of the results of heating an ideal specimen in a vacuum at high temperatures is the driving off of oxygen which leaves the crystal with an excess of zinc. The system presumably reaches equilibrium when a fraction of about 10^{-4} of the oxygen atoms have left. Since the crystal remains electrostatically uncharged, the oxygen which leaves must be neutral. The electrons which are left behind are normally bound in some way but may be freed thermally and may then conduct a current. The decrease of A with oxygen vapor pressure is explicable if heating the specimen in a vapor pressure of oxygen shifts the equilibrium fraction of excess zinc. Wagner and Schottky[20, 21] have given this process a reasonable interpretation in terms of principles of statistical mechanics. Thus the relation (5) may be explained semi-quantitatively in terms of the laws of mass action, as they are ordinarily applied to gaseous reactions.

In what physical form is the excess zinc present? According to Wagner there are two ways in which we may have deviations from ideal stoichiometric ratios. First, this may occur by having oxygen ions missing from ordinary oxygen sites. In this case the electrons left behind will occupy these sites at low temperatures. Second, the deviations may occur by having the excess zinc ions present in the lattice interstitially. The excess electrons will accompany these vacant ions at low temperature, essentially giving us interstitial zinc atoms. As in the other case, these zinc ions may be ionized thermally. The observed positive ion transport number strongly supports the second picture, since it indicates that the negative ions are practically unable to move through the lattice. Apparently we may conclude that the oxygen atoms leave the surface of the specimen when it is heated in a vacuum and that the zinc atoms which remain diffuse into the interstices of the lattice. This procedure is partly reversed when the oxygen vapor pressure is increased. Crystals which have the zincblende and wurtzite structures are very porous because of the low coordination number and leave ample room for interstitial atoms and ions.

The dependence of ϵ in (4) on oxygen vapor pressure indicates that the interstitial zinc atoms are not bound equally tightly and that the looser ones which leave the lattice most easily have smaller values of ϵ. A similar conclusion has been drawn for the case of Cu_2O by Engelhard.[22]

If we now assume that zinc oxide and zinc sulfide have analogous properties, we may explain the luminescence of pure zinc sulfide in the following way. The pure zinc sulfide which is formed by precipitation from solution has practically ideal structure and practically no excess of zinc atoms. Sulfur evaporates from these crystals when they are heated in a vacuum and the excess zinc atoms diffuse into the lattice. These atoms may be optically as well as thermally ionized. The recombination of an interstitial zinc ion and an electron gives rise to phosphorescence. The recombination should approximately obey an equation of the type (1).

Since the most efficient wave-lengths for exciting pure zinc sulfide lie in the ultraviolet and the emitted radiation lies in the blue, one might at first sight be inclined to say that the thermal activation energy for ionizing the interstitial atoms in zinc sulfide is so large that no semiconductivity may be expected at ordinary temperatures. This conclusion may be in error for the following reasons, aside from the Franck-Condon principle and the fact that ϵ in (4) must be less than half the optical excitation energy because of the bimolecular character of ionization. As we said above, the dependence of ϵ on oxygen vapor pressure in the case of ZnO indicates that all interstitial zinc atoms are not bound in the same way. Hence it is possible that (a) either most of the centers have a larger value of ϵ than those which ordinarily are responsible for conduction, or (b) the centers which have largest ϵ's have the largest cross section for optical ionization. Either

[21] Schottky and Wagner, Zeits. f. physik. Chemie **B11**, 163 (1931). A survey of these computational methods may be found in the review article by Nix and Shockley, Rev. Mod. Phys. **10**, 1 (1938).

[22] Engelhard, Ann. d. Physik **17**, 501 (1933).

or both of these possibilities may account for the coexistence of visible luminescence and a low value of ϵ in the same crystal.

C. Luminescence of copper activated zinc sulfide

The close similarity of the luminescent behavior of zinc sulfide activated by copper and pure zinc sulfide suggests that a similar mechanism is responsible for the luminescence in both cases. In view of *B*, we may postulate that the copper activated sulfide contains interstitial copper atoms. These are ionized by the light which stimulates both phosphorescence and photoconductivity, and the phosphorescent light is produced by the recombination of these ions and electrons.

What can be said about the energy required to ionize either interstitial zinc or copper atoms? The position of the normal states of free copper and zinc atoms relative to the levels of zinc sulfide are illustrated in the first and second columns from the left in Fig. 1. These diagrams show that the energies required to remove an electron from these atoms and place the electron in the conduction band are approximately 6.7 and 5 ev, respectively. The fact that the optical excitation energies of the phosphors are considerably less than these values indicates that the atoms are appreciably perturbed by being brought into the lattice.

One of the important questions which remain to be answered is the following: Why do the activating copper atoms enter interstitial rather than substitutional positions? If the copper atoms would prefer substitutional positions in the true equilibrium state, we must assume that interstitial diffusion takes place much more rapidly than substitution, in which case the copper activated phosphor is in a metastable state. However, it is not necessarily true that the copper atoms would prefer substitutional positions. This may be shown by the following schematic computation, which is patterned after the theory of Schottky and Wagner,[21] on deviations from ideal stoichiometric relations.

Let us consider a zinc sulfide crystal in which there are N lattice sites for zinc ions and let us add to this m copper atoms where $m \ll N$. We shall assume that n of these enter substitutional positions and $m-n$ enter interstitial ones, replacing zinc atoms which then appear in interstitial positions. We shall let ϵ_{Cu} and ϵ_{Zn} be the cohesive energies of the interstitial copper and zinc atoms and shall let $\Delta\epsilon_{sub}$ be the energy required to interchange a free copper ion and a bound zinc ion which is in a zinc site. This energy is composed of two terms: (1) The difference in cohesion of a copper ion and a zinc ion in a zinc site, and (2) the energy of 0.65 ev required to remove two valence electrons from a neutral copper atom and to place them on a zinc ion. The copper sulfide lattice is considerably different from the zinc sulfide lattice and its cohesive energy, referred to monatomic copper, is about 0.92 ev per molecule more stable than the ZnS lattice, referred to monatomic zinc. Mayer[23] has shown in the case of some monovalent halides that the relative stability of different lattice types is of the order of 1 ev per molecule. Hence we may conclude that $\Delta\epsilon_{sub}$ is probably positive and of the order of magnitude 1 ev.

We shall assume that the entropy which is gained by substituting n copper ions for n zinc ions is the mixing entropy

$$k \log \frac{N!}{n!(N-n)!} \leqq -kn \log \frac{n}{N}.$$

The entropy of $m-n$ interstitial atoms will lie between the value

$$-k(m-n) \log (m-n)/\rho,$$

associated with the possible permutations among ρ interstitial sites, and the value

$$-k(m-n) \log (m-n)/C+5/2k$$

for a perfect gas. Here

$$C=(2V/h^3)(2\pi\mu kT),$$

where V is the volume of the crystal and μ is the mass of the atoms. Fortunately both of these expressions lead to practically the same equilibrium value of n since the sum of the number of interstitial zinc and copper atoms is constant. The total relative free energy ΔA of the crystal is

$$\Delta A=(m-n)\epsilon_{Cu}+n\epsilon_{Zn}+n\Delta\epsilon_{sub} +kT[n \log (n/N)+(m-n) \log (m-n) +n \log n]+\alpha.$$

[23] Mayer, J. Chem. Phys. **1**, 327 (1933).

where α is independent of n. This is a minimum when

$$\frac{n^2}{(m-n)N}=\exp\left(\epsilon_{Cu}-\epsilon_{Zn}-\Delta\epsilon_{sub}\right)/kT.$$

The energy term $\epsilon_{Cu}-\epsilon_{Zn}-\Delta\epsilon_{sub}$ is the energy required to interchange an interstitial zinc atom and a substituted copper ion. We have estimated $\Delta\epsilon_{sub}$ roughly above, but it does not seem feasible to attempt an estimate of $\epsilon_{Cu}-\epsilon_{Zn}$. The condition which must be satisfied if n is to be small compared to m is that

$$\exp -(\Delta\epsilon_{sub}+\epsilon_{Zn}-\epsilon_{Cu})/kT$$

be small compared to m/N, which we shall take to be of the order of 10^{-4}. For $T\sim 1200$K, the temperature at which phosphors are ordinarily activated, this implies that the energy which is required to interchange an interstitial copper atom and a zinc ion must be greater than 2 ev. If this condition is satisfied most of the copper atoms will remain in interstitial positions. If it is not quite satisfied all interstitial copper atoms eventually should be replaced by zinc atoms, assuming $m/N\sim 10^{-4}$. In this case the copper activated luminescence should be replaced by the luminescence of the pure sulfide in the course of extended heating at high temperature.

Guntz[4] has pointed out that copper activated zinc sulfide which has been made nonluminescent by extensive nonhydrostatic pressing becomes light brown in color as a result of the pressing. This color, he estimates, is the same as that one would obtain by making a mechanical mixture of pure zinc sulfide and an amount of cupric sulfide which is chemically equivalent to the amount of copper present in the phosphor. This suggests that the copper is not present in the cupric form in the luminous material and that it reverts to this form when thermodynamical equilibrium is attained by pressing.

4. Conclusion and Summary

In conclusion it may be pointed out that the alkali halide phosphors and the zinc sulfide phosphors probably furnish the standard types for classifying most other phosphors. As yet it is not possible to say definitely to which class belong substances such as Zn_2SiO_4 (willemite) and $CaWO_3$, but it is hoped that experiments which will permit such a classification will be carried out in the near future.

A summary of the contents of this paper can be found in the abstract.

In conclusion I wish to thank Dr. N. T. Gordon and Mr. F. Quinlan for their collaboration in connection with some of the experiments described in this work.

A Determination of the Magnetic Susceptibilities of Certain Inorganic Complex Compounds

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A standard method used in the determination of the gyromagnetic effect has been so modified as to permit the determination of magnetic susceptibilities. Its use is suggested for the determination of the susceptibilities of complex compounds, since it utilizes weak fields, and also requires only a small amount (less than 0.5 g) of the material to be tested. The susceptibilities of some compounds containing NO have been measured.

WORK done by Pauling[1] and others has given an impetus to the determination of magnetic susceptibilities by showing that a knowledge of the susceptibility of a compound limits the number of structures which that compound may possess; in some instances a unique determination of structure is possible.

Since a great many of the complex compounds of the transition elements, to which these ideas are primarily applicable, can be prepared in only small quantities, we sought a method by which susceptibilities might be determined using only small quantities of material. Initially the use of weak fields was fortuitous. Subsequently we found that a number of compounds exist whose susceptibilities change from large and negative in the presence of weak fields to positive in the presence of intense fields. Further work is being done on susceptibilities in weak fields.

EXPERIMENTAL

The method here employed for determining magnetic susceptibilities consists in maintaining a suspended specimen in torsional vibration by the periodic imposition of a magnetic field of suitably adjusted intensity. A similar arrangement has been used in investigating the gyromagnetic effect, and was introduced by Einstein and de Haas in 1915. It has subsequently been developed by other workers, as for example Coeterier.[2]

The substance whose susceptibility is to be measured is suspended from a quartz fiber between the poles of an electromagnet. The specimen, which is in the shape of a cylinder whose length is large compared to its diameter, will experience a torque such as will tend to align it parallel to the field if it is paramagnetic, or perpendicular to the field if it is diamagnetic. The deflecting torque will be equal to the product of four terms: (1) the square of the field; (2) the susceptibility of the specimen; (3) a function of the angle between the axis of the specimen and the direction of the magnetic field; and (4) a function of the size and shape of the specimen. The measurement of the deflecting torque permits the calculation of (2) provided (1), (3) and (4) are known. However, (3) and (4) would be difficult to calculate for any container of an easily fabricated shape. On the other hand, (3) and (4) remain constant as long as the size and shape of the container, and the angle of deflection, remain constant. If one restricts oneself to the determination of relative susceptibilities, therefore, these quantities need not be known. This restriction at the same time obviates the necessity of calculating the absolute values of the deflecting torque, and of (1), the magnetic field. These may be taken as proportional to the angle of deflection, and the current in the electromagnet respectively.

Instead of determining the deflecting torque directly, the following procedure was used. The specimen was so set that in its equilibrium position, without the application of any field, its axis was at forty-five degrees to the direction of the magnetic field. The magnetic field was then impressed periodically in such a way as to build up oscillations. A mechanism to be described later ensured that the magnet would always be turned on and off at precisely the same angles.

[1] Pauling, J. Am. Chem. Soc. **53**, 1367, 3225 (1931).
[2] Coeterier and Scherer, Helv. Phys. Acta **5**, 217 (1932).

TABLE I.

R	70.0	80.0	100.0	120.0	150.0	200.0	300.0	400.0
O	39.90	35.05	28.05	23.40	18.70	14.05	9.30	7.00
RO	2793	2804	2805	2808	2805	2810	2790	2800

With a given current passing through the magnet, the oscillations would build up until the energy per cycle supplied by the magnet, $\int_{\theta_1}^{\theta_l} Ld\theta$, was equal to the energy dissipated per cycle by air damping. From then on, the specimen would oscillate with constant amplitude. Any change in the current through the magnet would change the magnetic field, and thereby change the energy input per cycle, and consequently the amplitude.

A comparison of the susceptibilities of two substances was effected by placing successively samples of each in the capsule and adjusting the resistance in the magnet circuit until the amplitudes were the same in each case. Since the magnetic field was applied over the same angles to a container of the same size and shape, the only variables were the susceptibilities, the masses, and the magnetic fields. Therefore:

$$m_1\chi_1+m_0\chi_0=k'/H_1^2=CR_1^2,$$
$$m_2\chi_2+m_0\chi_0=k'/H_2^2=CR_2^2,$$

where, since H is proportional to $1/R$, the reciprocal of the total resistance in the magnet circuit, this more convenient quantity is used. $m_0\chi_0$ is the product of mass and susceptibility for the empty capsule. Its value was determined by a separate experiment in which the empty capsule was oscillated with the same amplitude as was attained by the capsule containing the specimens. This gives the additional equation,

$$m_0\chi_0=k'/H_0^2=CR_0^2,$$

which permits the elimination of $m_0\chi_0$ from the preceding equations giving

$$m_1\chi_1=C(R_1^2\pm R_0^2),$$
$$m_2\chi_2=C(R_2^2\pm R_0^2),$$
$$\frac{m_1\chi_1}{m_2\chi_2}=\frac{(R_1^2\pm R_0^2)}{(R_2^2\pm R_0^2)},$$

where the plus sign is to be taken if the susceptibilities of the capsule and the contained specimen are of opposite sign, otherwise the minus sign.

The assumption that the magnetic field is proportional to the reciprocal of the total resistance in the circuit requires verification. For this purpose the magnetic field, as measured by a ballistic galvanometer and coil, was plotted against the total resistance in the circuit. A typical set of data is reproduced in Table I.

The maximum deviation from the mean is about $\frac{1}{2}$ percent, which indicates an accuracy sufficient for our purpose.

The magnet is of the conventional type, with a core of silicon steel. It is wound with 5100 turns of No. 20 copper wire, and when excited by a 40-volt d.c. generator with 250 ohms in series, gives a field of approximately 300 oersted. The generator is driven by a $\frac{1}{2}$ horsepower synchronous motor. In operation the magnet is connected to the generator through a set of variable resistances, a commutator, and a relay. The commutator is turned by a spring when an escapement mechanism is released on closing the relay; the commutator's alternately insulating and conducting segments permit current to pass only every other time that the relay is closed. The electrical circuit contains in addition two switches, by the proper operation of which the resistances in the circuit may be measured on a Wheatstone bridge.

The relay is closed when a spot of light reflected from a mirror mounted on the moving suspension falls on a photo-cell (Fig. 1). The activation of the photo-cell increases the grid potential of the thyratron sufficiently to permit the passage of the current which closes the relay. This mechanism ensures the synchronization of the periodic magnetic field with the torsional vibrations of the suspended capsule.

The suspension is a quartz fiber (Fig. 2). To this is attached a Pyrex glass rod on which are mounted two mirrors, one for visual observation of the amplitude of oscillation, and the other for reflecting the spot of light which actuates the

TABLE II.

		m	R	R_0	C
Mohr's salt	31.5	0.5298	441.5	69.17	0.836×10^{-10}
Ferric alum	29.4	.4655	398.9		$.834\times10^{-10}$
Potassium ferricyanide	6.94	.2052	111.0		$.834\times10^{-10}$

photo-cell. At the bottom of this rod is the cradle which carries the cylindrical specimen.

The apparatus was calibrated in the following way. Using the equation $m\chi=C(R^2\pm R_0^2)$, the constant C was determined by using three different salts—Mohr's salt, ferric alum, and potassium ferricyanide. The values obtained are shown in Table II.

All measurements were made at 27°C, using the susceptibilities as given in the *International Critical Tables* after correcting to 27°. The excellent agreement is certainly accidental, since weak fields (<300 oersted) were used. We consider our results reliable to 2 percent.

PREPARATION AND ANALYSIS OF COMPOUNDS

When dry NO is passed into a solution of metallic sodium in liquid ammonia, the original intense blue of the solution is rapidly bleached, and subsequent evaporation of the ammonia leaves a cake of very finely crystalline, colorless material. This material rapidly decomposes in water, giving off nitrous oxide, and leaving sodium hydroxide in solution. For this compound Zintl and Harder[3] have suggested the formula NaNO. Its reactions are entirely distinct from those of sodium hyponitrite, which has the same empirical formula. Molecular weight determinations have not been made, since it decomposes in all solvents so far tried.

The ferrous ammonium sulphate, ferric ammonium sulphate, and potassium ferricyanide were prepared and purified by standard methods, and these products were used in calibrating the apparatus.

The sodium nitroso-pentanitro-cobaltiate dihydrate, $Na_3[Co(NO)(NO_2)_5]\cdot 2H_2O$, was prepared by passing dried and purified nitric oxide into a flask containing a solution of one mole of cobaltous chloride, to which five moles of sodium nitrite were added at intervals, with constant stirring, and the whole kept at 0°C. The crystals, which formed after standing, were filtered off.

A similar method was used with the nitroso-pentammine cobalt dichloride, $[Co(NO)(NH_3)_5]Cl_2\cdot 5H_2O$, the chief difference being that the solid cobaltous chloride was placed in the reaction flask, and five moles of ammonium hydroxide were added at intervals at room temperature. The product was then filtered off.

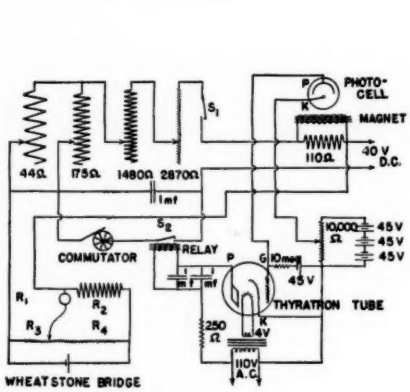

FIG. 1. Diagram of apparatus.

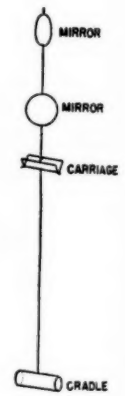

FIG. 2. Cradle and carriage.

In both preparations, care was taken to exclude air from the reaction flask.

The analysis of the first complex involves some unusual reactions, but appears to be accurate. Concentrated sulphuric acid was added to the complex in a stream of carbon dioxide, and the evolved nitric oxide reduced over hot copper. The nitrogen formed was collected and measured in a gas burette containing a strong potassium hydroxide solution. The copper oxide formed was reduced with hydrogen and the evolved water collected in a P_2O_5 tube. Sulphur dioxide was bubbled through the sulphuric acid residue, and a little water added to ensure complete hydrolysis. The evolved nitric oxide was treated as before. The equations for the analysis are:

$$2Na_3[Co(NO)(NO_2)_5]2H_2O+5H_2SO_4\rightarrow 2NO+4H_2O+2CoSO_4+10HNO_2+3Na_2SO_4$$

$$10HNO_2+10HOSO_2OH\rightarrow 10HOSO_2ONO+10H_2O$$

$$10HOSO_2ONO+10H_2O+5SO_2\rightarrow 10NO+15H_2SO_4$$

[3] Zintl and Harder, Ber. **66B**, 760 (1935).

TABLE III.

$Na_2[Co(NO)(NO_2)_5]\cdot 2H_2O$	THEORY	EXPERIMENTAL
Weight of N_2 from NO	0.00165	0.0016
Weight of N_2 from NO_2	.00827	.0082
Weight of water of crystallization	.0503	.0502

TABLE IV.

$[Co(NO)(NH_3)_5]Cl_2\cdot 5H_2O$	THEORETICAL	EXPERIMENTAL
Weight of N_2 from NO	0.0272	0.0268
Weight of NH_4Cl formed	.2077	.2024
Weight of water of crystallization	.1398	.1396

The results of the analysis are tabulated in Table III.

The analysis of the second complex was made by heating the compound mildly in a stream of carbon dioxide, collecting the ammonium chloride and water formed, and reducing the evolved nitric oxide to nitrogen as before. The ammonia evolved was absorbed by bubbling the gases through concentrated sulphuric acid The equations for the analysis are:

$$[Co(NO)(NH_3)_5]Cl_2\cdot 5H_2O\rightarrow NO+2NH_4Cl+3H_2O+3NH_3+Co(OH)_2$$

$$Co(OH)_2+CO_2\rightarrow CoCO_3+H_2O.$$

The results of the analysis are tabulated in Table IV.

As an additional identification, the nitroso-pentammine complex was refluxed with dilute and concentrated hydrochloric acid, to form the pink aquo-pentammine and the red violet chloro-pentammine complexes, respectively.

RESULTS OF MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Of the three compounds whose susceptibilities were measured, only one, $[CoNO(NH_3)_5Cl_2]\cdot 5H_2O$, was paramagnetic in weak fields. The data for this compound are given below.

m	R	R_0	C
0.2839	271.7	69.17	0.834×10^{-10}.

Substituting these values we obtain 23.1×10^{-6}. This value for the susceptibility indicates between two and four unpaired electrons, in apparent contradiction to the value quoted by Pauling, which indicates almost exactly two. Possible explanations of this discrepancy might be (1) the weak fields with which our measurements were made, or (2) the different number of molecules of water of hydration which our compound contained.

NaNO is diamagnetic at all field strengths attainable with our apparatus.

The compound $K_3[CoNO(NO_2)_5]$ is apparently a transition between the two previous cases. It is diamagnetic in weak fields, becoming gradually paramagnetic as the field strength is increased. This unexpected variation of susceptibility with field strength requires a modification of apparatus which is now being made.

We would like to suggest tentatively the following explanation for the susceptibilities of these three compounds. When NO enters into combination with a sufficiently electropositive atom or radical, the NO is actually reduced to a NO^- ion with the structure $:\dot{N}::\dot{O}:$. This occurs with the compound NaNO. When the combining radical, as in $Co(NH_3)_5$, is less electropositive the electron structure is that suggested by Pauling, in which the NO group contains two three electron bonds. Finally, the NO in the compound $K_3[CoNO(NO_2)_5]$ represents transition between these two extremes.

The Energy and Entropy of Activation of the Reaction Between Nitric Oxide and Chlorine[1]

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Following a discussion of the concept of entropy of activation and methods for its calculation, it is shown that the energy of activation of the formation of nitrosyl chloride from nitric oxide and chlorine is temperature dependent and permits an evaluation of the entropy of activation. A critical analysis is made of previous work.

THE concept of entropy of activation was first introduced by Kohnstamm,[2] Scheffer[3] and Brandsma,[4] but it was not given due consideration until La Mer[5] pointed out the necessity for its consideration in interpreting reaction kinetics, especially in solution.

Consider the reaction

$$A+B=C+D.$$

The velocities of the forward and reverse reactions, V_1 and V_2 are given in terms of concentrations by

$$V_1=k_1C_AC_B; \qquad V_2=k_2C_CC_D,$$

where k_1 and k_2 are the velocity constants of the forward and reverse reactions. At equilibrium,

$$V_1=V_2 \quad \text{and} \quad F_1=F_2,$$

where F_1 and F_2 are the free energies of reactants and resultants respectively. At any other point in the reaction, either $V_1>V_2$ when $F_1>F_2$ or $V_1<V_2$ when $F_1<F_2$. The analogous behavior of velocity and free energy is suggestive of a correlation. For the following discussion, free energy will be defined by

$$F=E-TS+RT=E-TS^0+RT+RT\ln C$$
$$=F^0+RT\ln C,$$

where E, S and T are energy, entropy and temperature, respectively; S^0 is the entropy in calories per degree per mole in the standard state of one mole per cc, F^0 is the corresponding free energy in the standard state and C is the concentration in moles per cc. The free energy of the reactants is then

$$F_1=F_A+F_B=F_1^0+RT\ln C_AC_B,$$

whence $C_AC_B=\exp(F_1-F_1^0)/RT$

or, from above,

$$V_1=k_1\exp(F_1-F_1^0)/RT=C_1'\exp F_1/RT$$

and $$V_2=k_2\exp(F_2-F_2^0)/RT=C_2'\exp F_2/RT.$$

At equilibrium the velocities and free energies being equal, the constants C_1' and C_2' are also equal but are not necessarily universal constants, as is easily shown. Substitution for the free energy gives

$$V_1=C_1'\exp(F_1^0/RT)\cdot C_AC_B,$$

whence $k_1=C_1'\exp(F_1^0/RT)$.

If now C_1' were a universal constant, it would be possible by measuring k_1 at various temperatures to determine absolute values of free energy. Since this is impossible, C_1' must contain an energy and entropy magnitude such that one can determine only free energy differences. If this free energy magnitude be represented F_x and taken out of the constant C_1' leaving a residual constant C_1'', whence

$$C_1'=C_1''\exp(-F_x/RT),$$

the velocity may be expressed:

$$V_1=C_1''\exp(F_1-F_x)/RT$$
$$=C_1''\exp(-\Delta F_1/RT).$$

This equation is in agreement with the Arrhenius hypothesis if F_x be recognized as the free energy of the activated complex.

[1] An abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, April, 1938.

[2] Kohnstamm and Scheffer, Verslag. Akad. Wetenschappen, Amsterdam **19**, 878 (1911).

[3] Scheffer and Brandsma, Rec. trav. chim. **45**, 522 (1926).

[4] Brandsma, Rev. trav. chim. **47**, 94 (1928); **48**, 1205 (1929).

[5] V. K. La Mer, J. Chem. Phys. **1**, 289 (1933).

This leads to an interesting point. Comparison of the free energies of reactants and resultants is logically made in the standard state where for the complex X,

$$F_x = F_x^0 + RT \ln C_x,$$

F_x^0 being a function of temperature and $RT \ln C_x$, a function of temperature and concentration. The velocity constant k_1 thus becomes from above:

$$\begin{aligned} k_1 &= C_1' \exp (F_1^0/RT) \\ \text{or} \quad \ln k_1 &= F_1^0/RT + \ln C_1' \\ &= (F_1^0 - F_x)/RT + \ln C_1'' \\ &= (F_1^0 - F_x^0)/RT + \ln C_1'' - \ln C_x \\ &= (F_1^0 - F_x^0)/RT + \ln C_1 \\ &= -\Delta F_1^0/RT + \ln C_1 \\ &= -\Delta E_1/RT + \Delta S_1^0/R + \ln C_1, \end{aligned}$$

where C_1 includes the concentration of the complex X and the universal constant C_1'':

$$C_1 = C_1''/C_x.$$

Similarly for the velocity constant of the reverse reaction:

$$\ln k_2 = -\Delta E_2/RT + \Delta S_2^0/R + \ln C_2,$$

where $C_2 = C_2''/C_x$.

C_1'' and C_2'' are universal constants and therefore equal. If C_1 and C_2 are to be equal, then C_x must be a constant for both the forward and reverse reaction. It must therefore be the equilibrium concentration of the intermediate complex.

This is as far as thermodynamics will go in the interpretation of reaction kinetics. The exact nature of the universal constant, C, must be determined empirically or by some hypothetical mechanism. Posthumus,[6] Rodebush[7] and La Mer[8] have attempted to apply collision theory, but are unable to obtain the temperature dependent universal frequency which not only relates the specific rates of reversible reactions, but also serves as a quantity common to all reactions. This is reflected in La Mer's inability to separate the entropy term from the frequency of collisions; an inability to calculate entropies solely from the temperature dependence of the energy of activation, since it is only when the standard states are considered that one obtains a true entropy term and the universal frequency.

The activated complex theory of Eyring[9] appears to provide the simplest approach to this universal frequency, wherein the rate of reaction is controlled by the frequency of passage of activated complex molecules over a potential barrier. If the equilibrium constant, K, between reactants and activated complex be expressed in the conventional units and the frequency of passage over the barrier be expressed as the number of complexes in a length $h/(2\pi m_x kT)^{\frac{1}{2}}$ rather than one centimeter of the barrier, the universal frequency is kT/h where, k, is the Boltzmann gas constant, h, is Planck's constant and, T, the absolute temperature. Then

$$RT \ln K^{\ddagger} = -\Delta F^0 = -\Delta E + T\Delta S^0,$$

whence $$\ln k_1 = \ln kT/h - \Delta E/RT + \Delta S^0/R.$$

From this equation and a knowledge of velocity constants over a sufficiently wide temperature range, entropies may be calculated.

The applicability of the Arrhenius equation, with its inherent assumption of a constant energy of activation, indicates that for most reactions the temperature range over which the reaction may be conveniently followed is too small, although Kassel[10] has drawn attention to Bodenstein's[11] actual findings in the hydrogen iodide decomposition where the energy of activation increases at the rate of about 35 cal./degree. It was thought that the formation of nitrosyl chloride with its small temperature coefficient would permit reaction velocity determinations over a very extended temperature range. However, precisely because of the increasing temperature coefficient, with increasing temperature an upper limit of 300°C was set by the experimental arrangement used.

The reaction has already been studied very extensively[12] but with little consistency among

[6] K. Posthumus, Rec. trav. chim. **52**, 241 (1933).
[7] W. H. Rodebush, J. Chem. Phys. **1**, 440 (1933); **4**, 744 (1936).
[8] V. K. La Mer, reference 5. Also J. Am. Chem. Soc. **57**, 2662, 2674 (1935).
[9] H. Eyring, J. Chem. Phys. **3**, 107 (1935) et. seq.
[10] L. S. Kassel, *Kinetics of Homogeneous Gas Reactions*, A. C. S. Monographs No. 57 (1932), p. 151.
[11] M. Bodenstein, Zeits. f. physik. Chemie **29**, 295 (1898).
[12] Kiss, Rec. trav. chim. **42**, 112 (1923); M. Trautz, Zeits. f. anorg. allgem. Chemie **88**, 285 (1914); Trautz and Wachenheim, ibid. **97**, 241 (1916); Trautz and Heng-

the results of various workers, for reasons which will be discussed later. The position of equilibrium is well known from the work of Trautz and Wachenheim[13] and of Dixon.[14] By studying both the decomposition and the formation of nitrosyl chloride, correlating the two by means of the equilibrium data, it has been possible to cover the temperature range from −25°C to 300°C.

Experimental

Formation of nitrosyl chloride

Since the reactions involve a volume change the rates can be followed manometrically. A Bodenstein quartz spiral was used as a null instrument for this purpose, being sensitive to a pressure difference of 0.01 mm mercury. The reaction vessel, also of quartz, was connected to the NO and Cl_2 reservoirs through glass bellows valves of the Bodenstein type using fused silver chloride seats. The gases were therefore never in contact with mercury or grease and could not become contaminated. Chlorine was obtained pure by fractional distillation of tank chlorine. The nitric oxide was obtained by the action of mercury on lead chamber crystals in concentrated sulphuric acid. For the higher temperature a nichrome resistance furnace was used, temperatures being measured with a platinum resistance thermometer. For the lower temperatures, a concentrated aqueous calcium chloride solution cooled with powdered solid carbon dioxide, was used in a large bath. In all cases the temperature was constant to within ±0.3°.

The rate of reaction is given by

$$2NO+Cl_2=2NOCl,$$
$$d(NOCl)/dt=k_3(NO)^2(Cl_2)-k_2(NOCl)^2,$$

where k_2 and k_3 are the velocity constants of the bimolecular reverse reaction and third order forward reaction. The equation was used in the approximate form:

$$\Delta(NOCl)/\Delta t=k_3(NO_{Av})^2(Cl_{2Av})-k_2(NOCl_{Av})^2,$$

the constants being related with the equilibrium constant as follows:

$$k_3/k_2=(NOCl)^2/(NO)^2(Cl_2)=K,$$

whence

$$k_3=\frac{K\Delta(NOCl)}{\Delta t[K(NO_{Av})^2(Cl_{2Av})-(NOCl_{Av})^2]}.$$

The observed pressures were converted directly into concentrations in moles per cc using the ideal gas law. Total concentration was plotted against time and the initial concentrations were obtained by extrapolation to zero time. It should be noted that the chlorine was usually the first gas admitted into the reaction vessel. The initial partial pressure of this is therefore accurately known. The initial partial pressure of the second gas admitted was obtained from the extrapolation. The average values in the above equation were taken as the arithmetic mean of the concentration at the beginning and end of the time interval Δt, calculated from the smoothed curve of the total concentration-time plot. Table I presents the complete data for one experiment.

In Table II is presented a summary of the experiments performed.

It will be observed from Table I that k_3 shows no trend throughout the experiment. In Table II the actual values of k_3 differ from the mean by less than ±5 percent. Variation of the relative concentrations of nitric oxide and chlorine has no effect on the value of the rate constant nor on the constancy of the values in any one experiment. The reaction is truly third order. This is also borne out by the recent work of Krauss and Saracini, but is contrary to the conclusions of Trautz and his collaborators who attempted to prove that the mechanism of the reaction involved the molecule $NOCl_2$ as an intermediate by observing rising constants when excess of chlorine was used and falling constants with excess nitric oxide. A critical analysis of all their data shows the presence of a number of errors.* In many cases no account was taken of the reverse reaction. In others, the constants were calculated from zero time to time, t, during the reaction, which puts an undue emphasis on the initial concentrations. In still others, there is an unjustifiable averaging of scanty data.

lein, ibid. **110**, 237 (1920); Trautz and Schlueter, ibid. **136**, 1 (1924); Krauss and Saracini, Zeits. f. physik. Chemie **178A**, 245 (1937).

[13] M. Trautz and F. Wachenheim, reference 12.

[14] J. K. Dixon, Zeits. f. physik Chemie, Bodenstein Festband, 679 (1931).

* See original thesis, I. Welinsky, New York University, 1938.

TABLE I.

TEMP. 61.0°C INITIAL Cl_2 60.1 MM (OBS.) INITIAL NO 127.7 MM (EXTRAP.)

OBSERVED		INTERPOLATED		
TIME (SEC.)	TOTAL PRESS. (MM)	TIME	TOTAL CONC. (MOLE/CC)	k_3 ($CC^2/MOLE^2/SEC.$)
60	185.1	0	9.010×10^{-6}	
105	183.8			3.52×10^7
165	182.2	2×10^2	8.686	
230	180.6			3.77
325	177.4	4	8.435	
380	176.6			3.66
435	175.3	6	8.248	
540	172.6			3.72
600	171.6	8	8.096	
690	170.3			3.79
795	168.6	10	7.970	
945	166.8			3.77
1050	164.4	12	7.865	
1230	163.1			3.64
1360	162.8	14	7.778	
1515	161.3			3.79
1650	159.6	16	7.700	
1915	158.1			3.74
2165	156.6	18	7.632	
				3.84
		20	7.570	
			Mean	3.73×10^7

The effects of these errors is shown in Table III, which presents some of the values calculated by Trautz and his co-workers and the values recalculated from their observed data in the manner described above.

It must be noted that the recalculated values in Table III are themselves good constants for each run and not the result of any extensive or unjustified averaging. The falling or rising trends of velocity constants claimed by Trautz as indicative of an intermediate reaction are to be found only in his own work and in that with Schlueter. The data by Trautz and Wachenheim and by Trautz and Henglein show no trends and none are claimed by them. That the trends claimed in his own work are in every case fictitious may be illustrated by some examples. Trautz's Table I as recalculated gives the following constants:

Trautz Table I.

281.7°K $P_{Cl_2}=51.4$ mm $P_{NO}=129.6$ mm

Time (sec.)	k_3
600	1.15×10^7
800	1.16
1000	1.15
1200	1.08
1400	1.04
1600	1.03
1800	1.10

TABLE II.

TEMP. °C	Cl_2 (MM)	NO (MM)	k_3	k_3 (MEAN)
−25.0	73.3	138.7	0.430×10^7	0.404×10^7
−25.0	50.5	144.0	.387	
−10.0	79.7	140.8	.661	.632
−10.0	75.4	143.1	.603	
0.0	67.9	120.2	1.004	
0.0	101.3	100.1	.868	.897
0.0	101.2	104.3	.897	
0.0	99.4	100.5	.883	
22.0	52.8	158.5	1.60	
21.5	101.8	101.0	1.58	1.597
22.0	69.3	136.5	1.68	
22.0	54.2	106.5	1.53	
27.5	43.5	82.5	1.70	1.70
60.0	99.7	116.3	3.37	3.55
61.0	60.1	127.7	3.73	
100.0	73.8	69.8	7.87	8.35
100.0	75.7	126.2	8.83	
146.0	59.6	63.3	20.13	18.35
146.0	47.3	76.5	18.57	
196.0	50.3	52.5	49.1	45.8
196.0	39.2	67.5	42.6	
203.0	65.2	69.2	45.3	45.3

Trautz's conclusion that excess NO gives falling constants is obviously not justified. Again, Trautz's Table 14 when recalculated is as follows:

Trautz Table 14.

451.1°K $P_{Cl_2}=76.1$ mm $P_{NO}=67.4$ mm

Time (sec.)	k_3
400	2.99×10^8
600	3.20
800	3.00
1000	2.94
1200	2.92

Here chlorine is in excess and the values are still constant within the experimental error. Actually Trautz claims a falling constant from 3.65 at 270 sec. to 3.10 at 960 sec.

The newer data by Trautz and Schlueter, which are supposed definitely to substantiate the suspected trends claimed in the earlier work, are based upon measurements made when the reaction was more than half completed. Krauss and Saracini also point out the scantiness of these data and the impossibility of attempting to recalculate constants from them. Furthermore, the data of Trautz and Schlueter are not self-consistent. For example, on page 22 three

experiments are reported. Experiment 20a, with excess NO shows the falling constants. 20b, with excess Cl_2 shows also falling constants, whereas by their theory they should rise, and finally 20c with excess NO shows good constants, whereas they should fall. In other words, their constants merely deviate from a mean by their normal experimental error, which appears to have been rather large.

With the exception of the Schlueter data, therefore, the work of Trautz and his co-workers really indicates the reaction to be truly third order and the agreement obtained upon recalculation of the third order constants with those here found is mutual confirmation of the validity of both.

The manner in which the data of the various investigators agree when correctly calculated is shown in Fig. 1. The curve has been drawn through the authors' data. The points referred to as decomposition were calculated from the equilibrium constant and the observed rate of decomposition of nitrosyl chloride. The two points of Kiss are the results of two separate investigations carried out ten years apart. Their agreement is good and the work shows none of

TABLE III.

TEMP. °C	k_3	k_3 (RECALC.)
146.2	21.35×10^7	16.51×10^7
146.2	23.55	17.70
168.5	31.15	29.40
178.0	36.50	30.10
0.0	1.100	.767
0.0	1.018	.854
0.0	1.002	.846
0.0	1.106	.810
18.0	1.906	1.37
161.1	20.4	22.45

the apparent anomalies reported by Trautz. The values obtained by Krauss and Saracini are consistently high and it is difficult to account for the discrepancy. It must be noted, however, that their work does not show the good internal consistency that is shown in the present work. Their values fall on a very good straight line which would intersect the indirect values at 150°C. Such a break in the curve is not to be expected.

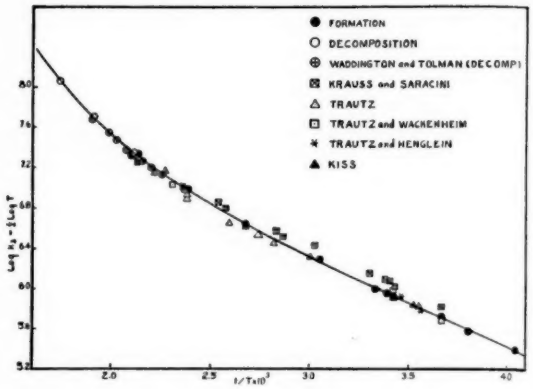

FIG. 1.

Decomposition of nitrosyl chloride

The nitrosyl chloride was prepared by the action of pure NO_2 on moist potassium chloride and purified by repeated distillation at −45°C, the first and last fractions being discarded in each case. The same reaction system already described was used; the nitrosyl chloride being connected to the reaction chamber through a greaseless glass bellows valve. The procedure was identical with that previously mentioned, the velocity constants of formation being calculated in the same stepwise manner. Save at the highest temperature (300°C) the extrapolation to zero time in order to obtain the initial pressure is easily made. At 300°C an approximate extrapolation was first made and the constants calculated therefrom. If the extrapolation was correct, the constants calculated showed neither rising nor falling trend. If such a trend was found, various possible extrapolations were tried until constancy was obtained. The fact that the constants so found agree for different experiments justifies the mode of calculation. Table IV contains the results obtained.

The agreement with the data of Waddington and Tolman[15] is good. Fig. 1 shows how well the formation and decomposition data agree.

Energy of activation

From the curvature shown in Fig. 1, it is obvious that the energy of activation is steadily increasing with temperature. Using the approxi-

[15] Waddington and R. C. Tolman, J. Am. Chem. Soc. **57**, 689 (1935).

TABLE IV.

TEMP. °C	P_0 MM	k_2 (CC/MOLE/SEC.)	$k_3=k_2K$ (CC^3/MOLE^2/SEC.)
200.0	144.2	78.0	4.74×10^8
200.0	158.5	74.3	4.51
250.0	99.5	1109.0	11.72
250.0	78.2	973.0	10.30
250.0	43.6	1109.0	11.72
250.0	40.4	1102.0	11.65
300.0	21.9	10320.0	25.9
300.0	23.5	9170.0	23.0
300.0	20.0	10750.0	26.9

TABLE V.

TEMP. INTERVAL °C	ΔE (CAL.)
−25– 0	3730
0– 50	4000
50–100	4460
100–150	5360
150–200	6400
200–250	7880
250–300	9860

mate equation,

$$\frac{\Delta(\log k_3-1/2\log T)}{\Delta(1/T)}=-\frac{\Delta E}{2.3R},$$

the values given in Table V were calculated. It is apparent that, even taking into account the variation of the collision frequency with temperature still leaves a value for the energy of activation which rises with increasing temperature. Kassel[16] has shown that collision theory cannot account for the observed rate of this reaction by a factor of 10^6 even at the highest temperature, and the discrepancy is even larger at lower temperatures, where the energy of activation is smaller. Gershinowitz and Eyring,[17] using the data of Trautz and Kiss to give a value for E_0, the energy of activation at the absolute zero, of 4780 cal. per mole, proceed thence to calculate the velocities at various temperatures by Eyring's method. The calculated values are lower than the observed by a factor of seven or eight. It is significant that the data in Table III would give a value of 4100 cal. using the method they adopted.

[16] L. S. Kassel, J. Phys. Chem. **34**, 1777 (1930).
[17] Gershinowitz and Eyring, J. Am. Chem. Soc. **57**, 985 (1935).

TABLE VI.

TEMP. INTERVAL °C	ΔE (CAL.)	ΔS^0 (CAL./DEGREE)
	FORMATION	
−25– 0	3,970	−12.85
0– 50	4,240	−11.32
50–100	4,900	−9.17
100–150	5,650	−7.80
150–200	6,950	−4.99
200–250	8,420	−2.08
250–300	10,300	1.33
	DECOMPOSITION	
150–200	22,700	−2.73
200–250	25,800	3.47
250–300	28,300	8.04

To calculate entropies of activation, the energies of activation are first calculated, not as for the collision theory, but from a direct plot of log k_3 against $1/T$, and then applied in the equation previously derived:

$$\ln k_3=\ln kT/h-\Delta E/RT+\Delta S^0/R.$$

Table VI lists the results so obtained for both the formation and decomposition of nitrosyl chloride. It is interesting to note that the energy of activation at the absolute zero obtained by extrapolation of the above data is approximately 3500 cal.

In conclusion a word may be said in reference to the recent suggestion of Bodenstein[18] concerning a mechanism for the reactions of nitric oxide with oxygen, chlorine and bromine involving as a primary step the formation of a dimer $(NO)_2$ in every case. Assuming a heat of dimerization of 4000 cal., he has accounted for the decreasing rate of the $NO-O_2$ reaction and the slowly increasing rates of the other two reactions with increasing temperature. It is well known that for the $NO-O_2$ reaction the plot of log k_3 against $1/T$ is noticeably curved at the higher temperatures. On Bodenstein's mechanism this could be accounted for by a varying heat of dimerization with varying temperature depending on the relative heat capacities of the monomer and dimer of NO. It is significant that the results here found for nitric oxide and chlorine show a more marked change in curvature at higher, than at lower temperatures and that the more marked curvature appears to set in at

[18] M. Bodenstein, Helv. chim. Acta. **28**, 743 (1935); Zeits. f. physik. Chemie **A175**, 294 (1936).

approximately the same temperature range for both reactions. This would appear to constitute a further argument in favor of Bodenstein's mechanism.

The data for the entropy of activation given in Table VI covering the temperature range 150–300°C, the range covered by direct measurement of both the formation and decomposition, give by graphical interpolation a value of 6.1 for the entropy change of the reaction at 250°C. This may be compared with the value of 6.28 obtained by calculation from the entropies of nitric oxide,[19] chlorine[20] and nitrosyl chloride.[21] The agreement is very satisfactory.

[19] H. L. Johnston and A. T. Chapman, J. Am. Chem. Soc. **55**, 153 (1933).
[20] W. F. Giauque and R. Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).
[21] F. P. Jahn, J. Chem. Phys. **6**, 335 (1938).

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The Solid-Liquid Equilibrium in Argon

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The method of investigating the equilibrium between solid and liquid phases, outlined in a previous paper, has been applied to argon. (In this method the intersections of the curves for the thermodynamic quantities $T(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T+P$, plotted as functions of the volume, are used to determine the conditions of equilibrium of the system.) Curves are found for the functions $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$, assumed dependent on volume and independent of temperature, which can reproduce with reasonable accuracy most of the melting parameters of argon at high pressures. The significance of these curves is discussed.

As a preliminary to a theoretical study of the solid-liquid equilibrium, it seems desirable to make as complete an analysis as possible of the available experimental material for a substance in which the factors determining this equilibrium are as simple as possible. Argon seems to be a suitable substance for such a study, since the data available are fairly extensive, and since the intermolecular forces are of the pure van der Waals type.

The method we use is that presented in a previous paper,[1] and is based upon the thermodynamic equation

$$T(\partial S/\partial V)_T=(\partial E/\partial V)_T+P. \qquad (1)$$

If the quantities $T(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T+P$ are plotted as functions of the volume, the points of intersection of these curves determine the volumes of phases which are in internal equilibrium at the given temperature and pressure. Such an equilibrium is a stable rather than an unstable one (i.e., corresponds to a minimum rather than a maximum of free energy) if $(\partial E/\partial V)_T+P$ is greater than $T(\partial S/\partial V)_T$ for values of the volume greater than the equilibrium volume. Of course, if there are two or more stable equilibria indicated in this way, in general one of them is the most stable; the condition that two phases be equally stable, and hence capable of coexistence, is that the area under the $(\partial E/\partial V)_T+P$ curve between the volumes corresponding to the two phases should be equal to the similar area under the $T(\partial S/\partial V)_T$ curve.

If the functions $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ changed very greatly with the temperature, such a method of analysis would be of little assistance. However, it seems probable that $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ can be considered, as a first approximation, as functions of the volume which are independent of the temperature, provided the temperature is sufficiently high so that quantization is not important. Inasmuch as the Debye characteristic temperature for argon is approximately equal to its normal melting point, it

[1] Rice, J. Chem. Phys. **5**, 492 (1937).

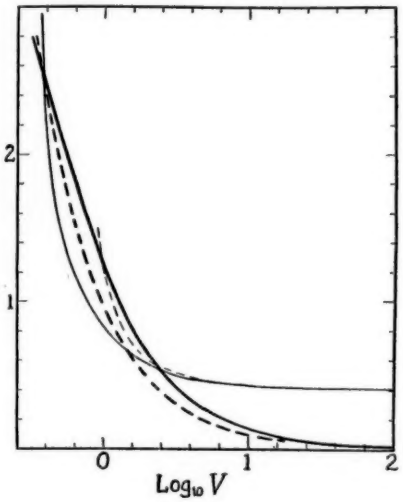

FIG. 1. Curves for large volumes. Heavy curve $(\partial E/\partial \log_{10} V)_T$; heavy broken curve approximation from Eq. (4) of Reference 1; light curve $T(\partial S/\partial \log_{10} V)_T$; light broken curve approximation from van der Waals equation, assuming b equals 1.5 times the critical volume. Energy and volume units as in Table I. Ordinates should be multiplied by 10^3.

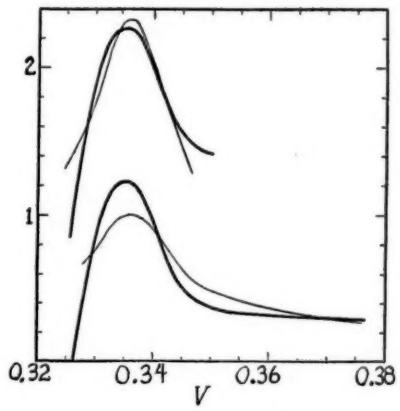

FIG. 2. Curves for small volumes. Heavy curves, $(\partial E/\partial V)_T+P$; light curves, $T(\partial S/\partial V)_T$. Units as in Table I. Ordinates should be multiplied by 10^4.

would seem that at temperatures equal to or above this melting point quantum effects can be neglected.[2]

In the cases of oxygen and nitrogen, the data on the transitions at normal pressures fix the $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ curves fairly well. This is largely because of the information furnished by the transitions between solid phases due to the setting in of molecular rotation in the solid state. In the case of argon there is no such transition point, so use has been made of Bridgman's data on the melting parameters at high pressures.[3] Specifically, we have tried to see to what extent curves for $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$, which are assumed independent of the temperature, can be used to correlate Bridgman's data. First, of course, we have made use of the data on the equilibrium between liquid and gaseous argon to construct curves for volumes larger than the volume of the liquid at the boiling point, just as was done with nitrogen and oxygen in our previous paper.[4] The results are shown in Fig. 1. The curves for smaller volumes were then made to join smoothly to these.

Trials were made with a variety of curves for both $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$. Curves for $T(\partial S/\partial V)_T$ for various values of T were plotted on transparent coordinate paper, and these could be moved vertically over the $(\partial E/\partial V)_T$ curve until the relation between them was such as to indicate that the conditions were correct for the coexistence of two phases[5] (assumed to be the liquid and solid phases). From the vertical displacement, the pressure at which the equilibrium between the two phases occurs could then be readily obtained. The temperature of the $T(\partial S/\partial V)_T$ curve then corresponds to the melting point at that pressure. The change of volume, ΔV, of fusion can also be readily obtained by noting the points of intersection of the $T(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T+P$ curves, and the change of energy, ΔE, on fusion can be obtained by measuring the area under the $(\partial E/\partial V)_T$ curve. The latter is not an entirely independent quantity, however.

In Fig. 2 we show the curves finally used. The $T(\partial S/\partial V)_T$ curve is shown for temperatures

[2] In reference 1 it was stated that the phenomenon of a transition point corresponding to fusion depended upon a characteristic decrease of the $(\partial S/\partial V)_T$ function at small volumes. It was suggested that this decrease was an effect of quantization. However, at the temperature of melting argon the entropy will have reached nearly its classical value, and it seems necessary to look for other causes for the decrease in the $(\partial S/\partial V)_T$ curve with decreasing volume.

[3] Bridgman, Proc. Am. Acad. **70**, 1 (1935); Phys. Rev. **46**, 930 (1934).

[4] See reference 1; the data used can be found in Landolt-Börnstein *Tabellen*. Most of it is collected in Rice, J. Chem. Phys. **5**, 353 (1937).

[5] The equality of the areas under the curves was first estimated by eye, with the aid, in the case of the curves finally used, of Dr. J. E. Magoffin. The final curves were then plotted on a larger scale and planimetered.

TABLE I. *Calculated and experimental values of the melting parameters. (Energies in calories per mole. The volume of a mole at the critical point, 75 cc, is taken as unity. The pressure units are consistent with these energy and volume units. All observed values from Bridgman.)*

Temp. (°K)	V_s		ΔV		Pressure		ΔE	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
83.9	0.3293	0.331	0.0437	0.0423	0	0	248	262
106.3	.3296		.0279	.0295	1710	1762	200	211
126.4	.3296	.326	.0196	.0226	3500	3520	174	182
162.0	.3291	.324	.0154	.0149	7070	7040	152	153
193.1	.3285	.323	.0134	.0112	10430	10600	138	142

83.9°K and 193.1°K, the lowest and highest used, and the $(\partial E/\partial V)_T+P$ curve is also shown. Since the former temperature is the normal melting point, the corresponding value of P is equal to (practically) zero.

In Table I we present a comparison of the values of P, ΔV, ΔE, and V_s, the volume of the solid which is in equilibrium with the liquid, calculated from the curves, with the data obtained by Bridgman. (We use the term liquid to describe the amorphous phase produced by the melting of the solid, even though the critical temperature be exceeded.)

It is also possible to calculate the volume of the liquid which is in internal equilibrium at various pressures, and any given temperature. These can be compared with data for pressures below that which causes the liquid to freeze, and even at slightly higher pressures, due to "super-compression." Calculations for 183.0°K are compared with Bridgman's data at the same temperature in Table II.

TABLE II. *Volume of the liquid at 183°K. (Critical volume of one mole of argon taken as unity. Pressure units as in Table I.)*

Pressure	Volume	
	Calc.	Exp.
5280	0.3572	0.357
6160	.3520	.352
7050	.3479	.346
7930	.3460	.3415
8800	.3440	.336
9680	.341	.332

Discussion

It will be seen from Table I that the proposed $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ curves reproduce the experimental data for P, ΔV, and ΔE at the various temperatures, with reasonable accuracy. However, the values of V_s given by the curves do not show as much trend with the temperature as do the experimental values. Bridgman remarked on the approximate constancy of V_s; however, actually it changes over the range considered, by some 2 percent, which can cause a relatively large change in the free or effective internal volume of a solid. It is possible that further experimentation with $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ would have produced a better fit; however, some effort failed to produce an improvement. The discrepancy would be removed if both $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ curves moved bodily to the left on the diagram at higher temperatures, but a shift sufficient to reproduce the observed trend seems rather unreasonable.[6] Table II also shows a discrepancy between observed and calculated values; this, however, is closely related to the discrepancies in the values of V_s, for it is clear that if there is a discrepancy in the volumes of the solid, without a corresponding discrepancy in ΔV, the discrepancy must reappear with the liquid. More disturbing is the discrepancy in the compressibility; this could probably be explained, however, by relatively slight trends in the $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ curves with temperature.

At certain pressures where the $T(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T+P$ curves nearly coincide over considerable ranges of the volume the calculated values of ΔV are very sensitive to small changes in the curves. Such small changes could readily occur with changing temperature, and could easily account for all the disagreement between experimental and calculated values in Table I, except for the case of V_s.

In spite of the difficulties discussed above, I believe that the $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ curves given in Fig. 2 cannot be far wrong. They present several features of interest, which, pending a complete theoretical treatment of the phenomena involved, seem worthy of some discussion.

[6] Professor Bridgman has very kindly communicated on this matter, and has stated that it is not impossible that the trend in his results is within experimental error. In this connection it should, however, be remarked that the volume of solid argon at around 20°K is given in the Strukturbericht as about 0.317 in our units, considerably too small to be accounted for by our curve, but the discrepancy is probably within the limits of experimental error.

In the first place we may make a comparison with the similar curves for nitrogen and oxygen. Of course, on account of the complications involved in the setting in of rotation in nitrogen and oxygen no direct comparison can be made of the $(\partial S/\partial V)_T$ curves. In the case of the $(\partial E/\partial V)_T$ curves it is of interest to note that the maximum is much broader in the case of nitrogen and oxygen than it is in the case of argon. It is not excluded that that may be to some extent due to inaccuracy in drawing the curves, but it hardly seems probable that it can be entirely due to this cause. Rather, it seems likely that the difference is associated with the fact that nitrogen and oxygen are diatomic while argon is monatomic. In the usual theory of van der Waals forces the attractive potential between molecules depends only on the distance between them and follows an inverse sixth power law. This theory, however, needs modification when the molecules are very close together. Corrections have been introduced which take the form of an eighth power attractive potential, but probably something more radical than that is needed. We might make the speculation that, with matter in bulk and very close packed, the correction depends upon the area of the surface of the molecule exposed to its neighbors. A diatomic molecule has more exposed surface than a monatomic molecule in comparison to the volume it occupies. A diatomic molecule should, therefore, have a relatively greater interaction with its neighbors; furthermore, as the substance expands the distance between the surfaces of neighboring molecules will increase less uniformly in the case of the diatomic molecule. Thus the force due to the pulling away of the molecules should be large over a greater range of volumes in the case of a diatomic molecule, and the maximum in the $(\partial E/\partial V)_T$ curve should be broader.

In agreement with these general ideas it may be mentioned that an attempt to account for the increase of energy of argon in the volume range between that of the solid and the liquid assuming an inverse sixth power attractive potential with coefficients of the right magnitude to give the correct energy of sublimation, was entirely unsuccessful no matter what repulsive potential was used.* The increase in the energy of the system at small volumes is entirely too great to be accounted for in this way, and would appear to indicate that the attractive force increases very rapidly at very small distances.[7] It should be possible, from the $(\partial E/\partial V)_T$ curve found here, to obtain the potential curve for a pair of molecules. Also, knowing the nature of the potential function for any molecule in the field of its neighbors, it should be possible to estimate its available free volume, and thus find the $(\partial S/\partial V)_T$ curve. The result could then be compared with the $(\partial S/\partial V)_T$ curve used here to reproduce the experimental data, and the comparison may throw some light on the question as to whether or not the excitation of "communal" entropy plays any appreciable role in the process of fusion.[8] It is proposed to continue the investigation along these lines in the near future.

* Powers for the repulsive potential as high as the 36th were considered.

[7] It should be noted that these calculations depend upon the assumption that corresponding to an increase is a uniform expansion of the lattice, an assumption which may need some further scrutiny, in view of the recent theories of holes.

[8] See the accompanying paper, J. Chem. Phys. **6**, 476 (1938).

On Communal Entropy and the Theory of Fusion

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The concept of "communal" entropy, introduced by Hirschfelder, Stevenson and Eyring, is further discussed in this paper. It appears from both theoretical and empirical considerations that the entropy of fusion of simple solids is *not* primarily concerned with the excitation of communal entropy. A discussion is given of the nature of communal entropy and its manner of excitation.

IN a recent paper Hirschfelder, Stevenson and Eyring[1] have introduced the concept of "communal" entropy, and have made the hypothesis that the principal contribution to the entropy of fusion of the simplest type of solid is due to the appearance of communal entropy. While they claim to have supported this hypothesis through certain experimental data, they have not given any very definite theoretical argument to sustain it. In view of the attractiveness of such an easily visualizable picture of the process of fusion some further analysis of the situation appears desirable. Unfortunately this analysis does not tend to confirm the hypothesis, at least in the simple form proposed by Hirschfelder, Stevenson, Eyring, and makes it at least improbable that the excitation of communal entropy plays any very important role in the phenomenon of fusion.

In order to make this analysis clear, it seems best to go back to first principles. We shall start with the consideration of a perfect gas. We shall suppose that we have one mole of atoms (let N be the number of atoms) confined in a volume V, this volume to be divided by partitions into r equal cells of volume V/r, each containing N/r molecules. Then we may set up the space part of the phase integral by raising V/r to the Nth power and multiplying by the number, $N!\div(N/r)!^r$, of arrangements of N molecules in r cells with N/r molecules in each cell, allowing for all possible exchanges of molecules from one cell to another. Thus we get a contribution, S_V, to the entropy

$$S_V = k \ln \frac{N!}{(N/r)!^r}\left(\frac{V}{r}\right)^N = k \ln N! - kr \ln (N/r)! + kN \ln (V/r), \quad (1)$$

where k is the Boltzmann constant. Evaluating the factorials by the Stirling approximation

$$S_V = kN(\ln N - 1) - kN(\ln (N/r) - 1) + kN \ln (V/r) = R \ln V, \quad (2)$$

where R is the gas constant. It is seen that this result is independent of the number of cells into which our volume is divided. However, this assumes that N/r is large enough to permit the use of the Stirling approximation. If, however, r should be equal to N, so that there is just one molecule in each cell, then the Stirling approximation would no longer be valid and we would have to set $(N/r)!=1$. We would then get

$$S_V = R(\ln V - 1) \quad (3)$$

and the entropy of one mole of gas would be less by an amount R. If, then we removed the partitions the entropy would increase by R, the "communal" entropy, just as stated by Hirschfelder, Stevenson and Eyring.

Let us investigate a little more closely the reason for this difference in entropy when we have partitioned the system into N cells. It arises because we have assumed that there is *exactly* one molecule in each cell. To change this situation we do not need to remove the partitions, but only to make an opening so that molecules can pass freely from one cell to another. Then, while the average number of molecules per cell is still one, there will be some cells with two or more molecules, and others with no molecules, and the number of molecules in any cell will change from time to time. It is the introduction of this possibility of fluctuations which causes the increase of R in the entropy. If, and only if, the cells were large enough so that they contained enough molecules to make

[1] Hirschfelder, Stevenson, and Eyring, J. Chem. Phys. **5**, 896 (1937).

fluctuations unimportant, opening the partitions would make no difference.[2]

In the case of a solid or liquid the situation is different in that the molecules themselves occupy most of the space and there is a relatively small free volume available for their motion. Since any molecule is excluded from the region immediately surrounding the center of another molecule, the question arises as to how effectively the free volume can be shared under various conditions due to fluctuations in the positions of the molecules. In other words, under what circumstances does the excitation of communal entropy occur? The answer of Hirschfelder, Stevenson, and Eyring may best be given in their own words: "As the system expands a point is reached when the neighbors no longer interlock and our partitions have just disappeared. At this point if a hole appears at anywhere in the system it can be transferred (made available) to any other point in the system without appreciable activation energy compared to kT. The system under such circumstances is a liquid. Thus a system on melting acquires communal sharing of volume and with it a communal entropy R." It is thus seen that they believe that the acquisition of communal entropy depends upon the ability of the molecules to change places among themselves.

However, the question of the sharing of the communal entropy has been definitely answered in one rather special, idealized case,[3] that of a one-dimensional gas consisting of solid, elastic, nonattracting spheres constrained to move along a fixed straight line of length l. If these spheres have a diameter of σ and there are N of them, then the available volume in the phase space is just the same as if there were N point molecules moving along a line of length $l-N\sigma$. Since $l-N\sigma$ corresponds to the free volume in this case, it is seen that this free "volume" appears to be completely shared. It is seen, further, that the sharing of the free volume is complete no matter how small $l-N\sigma$ may be; no question of ability of the molecules to exchange positions[3a] comes into the picture, and there is no evidence whatsoever that a very condensed and closely packed state of the system (as in the solid state) is at all inimical to the complete sharing of the free volume. The main point is that the molecules should be able to move back and forth enough to use all the available space.

Some difficulties arise when it is attempted to extend this to two or three dimensions. We might, for example, consider a two-dimensional square array composed of spherically symmetrical molecules arranged in lines. Lines of touching or nearly touching molecules extend in two directions at right angles to each other. However, since fluctuations can occur in either direction, some of these lines will be badly distorted or broken, thus complicating the situation. A recent observation by Gurney and Mott[4] enables us to avoid this difficulty. These authors showed that it is not necessary to consider a large number of molecules in order to get fairly accurate results. Thus if the space is divided into cells which contain exactly five molecules the communal entropy is nearly two-thirds excited (provided the sharing of free volume[4a] is complete), and if the cells contain 27 molecules the communal entropy is 90 percent excited. Let us consider a cell containing 9 molecules, as shown in Fig. 1. In as small a cell as this no molecule will be able to get much out of line, nor will the molecules in one row

[2] It is interesting that the incorrect evaluation of the factorial of a small number by use of Stirling's approximation is equivalent to allowing for fluctuations when they actually are excluded. It is to be noted that we refer here to the Stirling approximation in the less exact form,

$$\ln x! = x(\ln x - 1),$$

not the form,

$$\ln x! = \ln (2\pi)^{\frac{1}{2}} + (x+\tfrac{1}{2}) \ln x - x,$$

which holds reasonably well for much smaller values of x.

[3] Tonks, Phys. Rev. **50**, 955 (1936).

[3a] It is necessary to distinguish between the phrase, "change positions," and the phrase, "exchange positions." By a *change* in position we simply mean that the molecule moves away from its point of equilibrium; by *exchange* of position we mean that a definite rearrangement occurs so that the molecules have different neighbors than they did before the exchange. In calculating the phase integral for the linear system Tonks included all possible arrangements resulting from exchanges of position, as must be done in the Boltzmann statistics, and this has nothing to do with communal entropy. The question of importance for us is whether or not, in any given system, it is necessary in order for the communal entropy to be excited, that such exchanges should actually be able to occur in the course of the motion of the system as time goes on. It is the contention of the present paper that it is not necessary, but, if we understand them correctly, Hirschfelder, Stevenson and Eyring believe it is necessary.

[4] Gurney and Mott, J. Chem. Phys. **6**, 222 (1938).

[4a] Here, of course, we refer to the free volume *within* the cell containing only the five molecules.

FIG. 1. A group of nine in cubic packing.

interfere much with the motions of a molecule in an adjacent row. Thus the motion of the x and y coördinates of a molecule may be taken as independent of each other. This will be an especially good approximation if the free volume is relatively small; it is seen then from Tonks' calculation[3] that the available phase space is the same as if point-molecules occupied an area equal to $(l-N^{\frac{1}{2}}\sigma)^2$, where $N^{\frac{1}{2}}$ is the number of molecules per row and, as before, this may be interpreted as meaning that the free "volume" is completely shared. This can be extended to three dimensions.

With a triangular (close-packed) arrangement of spheres in two dimensions the situation is geometrically much more complicated, and it is not possible to give as satisfactory a discussion. It is not necessary, however, to consider a triangular array, such as shown in Fig. 2. We could, perhaps, consider as many as five molecules in a row to be in a single cell, there being, then, a fixed distance of motion in the y direction (perpendicular to the line of atoms) and sharing of free volume would occur due to the motion in the x direction. However, the motion in the x direction would, in reality, be affected by the positions of the molecules in the adjacent rows (notice that the boundary of the cell intersects adjoining atoms), and it is, furthermore, more difficult to formulate an expression for the free volume, making it hard to say whether this free volume is shared or not. However, and this is again the important point, there is no reason to believe that the degree of sharing of the free volume depends very much on the possibility of the molecules exchanging positions or on the relative size of the free volume as compared with the total volume. The closer the molecules are packed the nearer the adjacent row of molecules will be; thus the adjacent rows can interfere with each other more, but, on the other hand, less displacement in each row is required in order to effect a complete sharing of the free volume. Again the situation will not be very different in three dimensions.

The model we have used for a closely packed aggregate of spherical molecules suffers further in that it does not too closely resemble a real aggregation, since it neglects the forces of attraction and does not reproduce the forces of repulsion too well. Any discussion of the subject, to be at all complete, should include a consideration of these real molecular forces, but such a treatment promises to be very complicated. It is true that these forces may tend to cause a freezing out or, perhaps better, a "squeezing out" of communal entropy at small volumes. The excitation of communal entropy depends upon the ability of the molecules to change[3a] their positions; in other words, it must be possible for fluctuations to occur. Now fluctuations cause some molecules to approach each other while the distance between others increases. If the volume of the liquid is fairly large the approach of molecules means a decrease of potential energy, while the increase of the distance between them means an increase of energy. These two processes cancel each other's effects to some extent so fluctuations of the system do not represent states of particularly high energy. On the other hand, at small volumes, where the average intermolecular distance places neighboring molecules near the minimum of their mutual potential energy curve, any considerable change in distance will mean an increase in potential energy, so that fluctuations are thereby discouraged. However, this hindrance to the sharing of free volume would gradually fall off with increasing volume; just where it would cease to be effective we cannot be sure, and there is no way to connect it definitely with the process of fusion, and certainly there is nothing to indicate

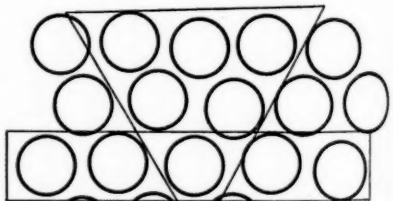

FIG. 2. Close packing, showing a triangular group of six and a linear group of five, in their appropriate cells.

that just the excitation of communal entropy is the principal contribution to the entropy of fusion, though it may contribute to some extent. Furthermore, if it is necessary to take complicated considerations regarding the intermolecular forces explicitly into account, the concept of communal entropy loses much of its meaning, and becomes more or less fused with ordinary entropy. It is my belief that the change with volume is more rationally presented as a continuous function of the volume, the nature of the function being the result of a combination of causes.[5]

I believe that the empirical evidence supports this point of view. It is true, as Hirschfelder, Stevenson, and Eyring have pointed out, that there are many substances whose entropy of fusion is approximately R. However, when we consider the entropy at various pressures, we note a continuous change in its value. Thus the entropy of fusion of argon, melting at 83.9°K and a pressure of 1 kg/cm² is 3.13 entropy units, while melting at 192.9°K and 6000 kg/cm² it is 1.35 entropy units.[6] Somewhere between it is just R, but I see no reason to suppose that the hypothesis of Hirschfelder, Stevenson, and Eyring should hold better at one temperature and pressure than another.

Quantization and the Freezing-Out of Communal Entropy

From the above discussion it might appear that, at least if intermolecular forces could be neglected, communal entropy should always be excited, but it may readily be seen that it must "freeze out" at low temperatures, in much the same way that other types of entropy freeze out, because the system is quantized. If we consider a system of spherically symmetrical molecules (e.g., rare gas atoms) at absolute zero, we can think of each molecule as being in its own special quantum state. These quantum states do not differ in the actual value of the energy, but only in their position in space. They are, nevertheless, perfectly distinct states and represent perfectly distinct regions in phase space, and obviously, no two molecules can occupy the same quantum state; hence communal entropy must be frozen out at the absolute zero.

It will be noted that in this discussion we have treated each molecule as though it were alone in its energy level, and have neglected the effect of the interactions of the molecules. This, however, will cause no error in the entropy at absolute zero; the entropy is as low as it can be in any case, and the system *as a whole* has just $N!$ energy levels of equivalent energy (corresponding to all possible exchanges of the N molecules if we use Boltzmann statistics, which is satisfactory for our purposes).

It is not easy to say at exactly what temperature this freezing-out of the communal entropy will occur. Since a substance like argon acts practically like a classical system at its melting point, it seems altogether doubtful that this process can be intimately connected with the phenomenon of fusion.

In closing it may not be without interest to note that the idea of communal entropy may be used to get the relation between the entropy of a solid and a hypothetical ideal gas at very low temperatures in a very direct way, and may thus serve as a means of obtaining the Sackur-Tetrode constant of the gas on the basis of the third law of thermodynamics.

[5] Rice, J. Chem. Phys. **5**, 492 (1937); and see the accompanying paper, J. Chem. Phys. **6**, 472 (1938).
[6] Bridgman, Phys. Rev. **46**, 930 (1934).

The Entropy of Ethyl Alcohol from Molecular Data and the Equilibrium in the Hydration of Ethylene

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The entropy and free energy of ethyl alcohol gas have been calculated from the molecular data at several temperatures on the basis of (*a*) free internal rotation, (*b*) restricted rotation (with potentials; about C−C bond = 3000, C−O bond = 10,000 calories). The latter values are in perfect agreement with those from the third law and from the equilibrium data on the hydration of ethylene.

I. INTRODUCTION

RECENTLY discrepancies have been found between entropies of nonrigid polyatomic molecules, calculated from the molecular data assuming free internal rotations, and those from thermal data down to liquid hydrogen temperatures and the third law of thermodynamics.[1–5] The discrepancy of about 2 e.u., per group capable of internal rotation, might be due to random orientation in the crystal at low temperatures, corresponding to a zero point entropy of 2 e.u., or to a force associated with potential barriers of about 3000 calories restricting the internal rotations.[1, 3] Kemp and Pitzer[3] have shown that restricting potentials are the cause of a discrepancy of 1.51 e.u. in the entropy of ethane at 298°K by considering the equilibrium in the hydrogenation of ethylene, a conclusion in agreement with the infra-red absorption spectrum[6] and the low temperature specific heats of the gas.[7]

Taken together these facts are convincing; but obviously, it is desirable to obtain similar evidence in other cases. The requirements are:

(a) Equilibrium constants for a reaction wherein the number of internally rotating groups is changed.

(b) Complete thermal data *down to liquid hydrogen temperatures.*

(c) Molecular data for each substance.

(d) An accurate value of ΔH close to the temperature of equilibrium.

Such a reaction is that involved in the vapor phase of hydration of ethylene.

$$C_2H_4(g)+H_2O(g)\rightleftarrows C_2H_5OH(g).$$

II. THE ENTROPY OF ETHYL ALCOHOL GAS FROM THERMAL DATA

Table I summarizes the calculation of the entropy of the hypothetically perfect gas at the normal boiling point and at 403.2°K from the best available calorimetric data. The entropy increase from 298.16°K was obtained by integration of the equation expressing the heat capacity data of Fiock, Ginnings, and Holton.[9]

TABLE I. *The calorimetric entropy of ethyl alcohol at 351.5°K and 403.2°K.*

	E.U./MOLE
0°K (cryst.)–298.16°K (liq.)[8]	38.4 ±.3
Liquid 298.16–351.5°K[9]	4.90±.005
Vaporization 9255/351.5[9]	26.33±.03
Entropy of actual gas at boiling point (351.5°K[11])	69.63±.3
Correction for gas imperfection[10]	.14
Entropy of ideal gas at boiling point	69.8 ±.3
0°K (cryst.)–298.16°K (liq.)[8]	38.4 ±.3
Liquid 298.16–403.2°K[9]	9.99
Vaporization 8034/403.2[9]	19.93
Entropy of act. gas at 403.2 and 5.682 atmos.	68.32±.3
Correction for gas imperfection[10]	.32
Entropy of ideal gas at 403.2°K and 5.682 atmos.[11]	68.64±.3
R ln 5.682	3.45
Entropy of ideal gas at 403.2°K and 1 atmos.	72.1 ±.3

[1] Aston and Messerly (a) J. Chem. Phys. **4**, 391 (1936). (b) J. Am. Chem. Soc. **58**, 2354 (1936).
[2] Kassel, J. Chem. Phys. **4**, 493 (1936).
[3] Kemp and Pitzer (a) J. Chem. Phys. **4**, 749 (1936). (b) J. Am. Chem. Soc. **59**, 276 (1937).
[4] Aston, Siller and Messerly, J. Am. Chem. Soc. **59**, 1743 (1937).
[5] See also Kistiakowsky and Wilson, J. Am. Chem. Soc. **60**, 494 (1938).
[6] Howard, J. Chem. Phys. **5**, 451 (1937).
[7] Kistiakowsky and Nazmi, J. Chem. Phys. **6**, 18 (1938).
[8] Kelley, J. Am. Chem. Soc. **51**, 779 (1929).
[9] Fiock, Ginnings, and Holton, Nat. Bur. Stand. J. Research **6**, 881 (1931).
[10] Calculated from thermodynamics and the modified Berthelot equation: $P_c=63.1$ atmos., $T_c=516.3$°K. ("I.C.T.").
[11] *International Critical Tables.*

III. The Entropy of Ethyl Alcohol from Molecular Data

(a) The vibrational entropy

The Raman Spectrum[12a, b] seems to contain lines corresponding to all but one of the nineteen modes of vibration. As only a partial normal coordinate treatment has been made,[12b] comparison with spectra of other molecules was resorted to. On this basis the following frequency assignment has been made

C−C−O skeleton: $\nu(\pi)$, 883; $\nu(\sigma)$, 1096; $\delta(\pi)$ 433:
CH_3 (internal): $\nu(\pi)$, 2930; $^2\nu(\sigma)$, 2930; $\delta(\pi)$, 1274; $^2\delta(\sigma)$, 1455:
OH (internal): ν, 3359
CH_2 (internal): $\nu(\pi)=\nu(\sigma)$, 2930; $\delta(\pi)$, 1274.
C−O−H (hydrogen angle variation): δ_1, (700).
CH_3-CH_2-O (hydrogen angle variation): $\delta_2\sim\delta_3$, 814; $\delta_4\sim\delta_5$, 1051; δ_6, 1455.

The nomenclature is as usual[13, 2, 4] for the inner frequencies of the groups. The frequencies δ_1, δ_2, δ_3, δ_4, δ_5, and δ_6, correspond to modes of vibration in which the angle of bonds holding hydrogen is changed relative to the whole molecule. At the same time the internal angles of the groups CH_3, CH_2, and OH are unchanged.[2, 3b]

The frequency δ_1 for OH bending is apparently absent from the Raman spectrum and for this its corresponding value in methyl alcohol has been used.[2] The assignment of the remaining five frequencies is largely a guess. As the result due to all six δ_i frequencies is about what would result if all were at 950 cm^{-1} (the corresponding average for ethane and ethylene),[14] no large error would be expected. The errors due to an extreme misinterpretation will be discussed presently.

Taking hc/k as 1.432 and R as 1.9869, the vibrational entropy and $-((F^0-E_0^0)/T)_{vib}$ are then calculated from Nernst's tables.

(b) The translational and rotational entropy

The distances and angles used were: CH =1.11A; OH=0.95A; CC=1.54A; CO=1.42A: <HCO=<CCO=<HCH=109° 28′; <COH =110°[2]. For the model in which the methyl and hydroxyl groups are rotating freely, the translational and rotational entropy was calculated by conventional methods.[15, 16]

Kassel has greatly simplified the method of Eidinoff and Aston, particularly in the case where symmetrical tops are attached to a rigid frame (see his Eq. (11)). However his Eq. (11) is obviously valid for any molecule with simple tops attached to a rigid frame, whether these be symmetrical or not. The only limitation is that these tops themselves must be rigid. If the attached rigid tops are not symmetrical the determinant in Eq. (11) of Kassel is a function of the variables α which represent the angular position of these tops. The rotational entropy is then given by

$$Q=(2\pi kT/h^2)^{s/2}(8\pi^2/\sigma)\int_0^{2\pi}\cdots\int_0^{2\pi}[R]^{\frac{1}{2}}d\alpha_1 d\alpha_2\cdots d\alpha_{s-3}, \tag{1}$$

where

$$[R]=K_1K_2\cdots K_{s-3}\begin{vmatrix}(yy)+(zz)-(\lambda\lambda) & -(xy)-(\lambda\mu) & -(xz)-(\lambda\nu)\\ -(xy)-(\lambda\mu) & (xx)+(zz)-(\mu\mu) & -(yz)-(\mu\nu)\\ -(xz)-(\lambda\nu) & -(yz)-(\mu\nu) & (xx)+(yy)-(\nu\nu)\end{vmatrix}.$$

Our choice of axes was dictated by other related problems so as to simplify the total labor. Initially, the y axis was taken to bisect the angle between the C−C bond and one of the CH bonds of the CH_2 group. The $x-y$ plane included both of these bonds.

The terms of (1) about parallel axes through the center of gravity $\times 10^{40}$ are:

[12] (a) Bolla, Zeits. f. Physik. **89**, 513 (1934); **90**, 607 (1934). (b) Cross and Van Vleck, J. Chem. Phys. **1**, 350 (1933).
[13] Bartholomé and Sachsse, Zeits. f. physik. Chemie **B30**, 40 (1935).
[14] Pitzer, J. Chem. Phys. **5**, 473 (1937).
[15] Eidinoff and Aston, J. Chem. Phys. **3**, 379 (1935).
[16] Kassel, J. Chem. Phys. **4**, 276 (1936).

TABLE II. *The entropy of ethyl alcohol from molecular data.*

	FREE ROTATION		RESTRICTED ROTATION	
T°K	351.5	403.2	351.5	403.2°K
S_{t+r}	69.44	70.80	61.13	62.30
S_v	3.53	4.29	3.53	4.29
S_r(CH_3) (3000 cal.)			2.5	2.8
S_r(OH) (10,000 cal.)			2.6	2.7
Total (less nuclear spin)	73.0	75.1	69.8	72.1
Calorimetric corrected to ideal gas state	69.8	72.1	69.8	
Discrepancy	3.2	3.0	0.0	—

$$(xx)=32.54-1.18\sin\alpha+1.29\sin^2\alpha,$$
$$(yy)=43.67+1.97\cos\alpha+0.86\cos^2\alpha,$$
$$(zz)=29.17-1.31\cos\alpha+0.42\cos^2\alpha,$$
$$(xz)=12.63-1.12\sin\alpha-0.35\cos\alpha+0.72\sin\alpha\cos\alpha,$$
$$(yz)=25.76-0.20\cos\alpha+0.59\cos^2\alpha,$$
$$(xy)=-28.14-0.49\cos\alpha+1.22\sin\alpha+1.03\sin\alpha\cos\alpha$$

(where α is the angle orienting the OH group),

$$(\lambda\lambda)=3.65\times10^{-40},\quad(\mu\mu)=2.26\times10^{-40},$$
$$(\nu\nu)=0.89\times10^{-40},\quad(\lambda\mu)=-2.58\times10^{-40},$$
$$(\lambda\nu)=0,\quad(\mu\nu)=-0.63\times10^{-40},$$
$$K_{OH}=1.32\times10^{-40},\quad K_{CH_3}=5.46\times10^{-40}.$$

The symmetry number is three.

It is necessary to integrate Eq. (1) graphically to obtain the partition function.

The rotational and translational entropy is

$$S_{t+r}=10/2\,R\ln T+11.194 \qquad (2)$$

and the "free energy"

$$-((F^0-E_0{}^0)/T)_{t+r}=10/2\,R\ln T+1.260. \qquad (3)$$

Table II (columns 1 and 2) summarizes the calculations of the total entropy (S_{t+r+v}) at the boiling point and at 403.2°K (130°C) on the basis of free rotation.

The discrepancy of 3.2 e.u. at 351.5°K and of 3.0 e.u. at 403.2°K will later be shown *not* to be due to random orientation in the crystal.

On the basis that the discrepancy is due to the incorrect assumption of free internal rotation, the potential hindering the rotation of the hydroxyl group was chosen to fit the data at 403.2°K. The method of Pitzer[17] was used, and from his work, the potential hindering the methyl group was taken as 3000 cal. For this calculation "s" in the first factor of Eq. (1) was taken as 3. The terms $\lambda\lambda$, $\lambda\mu$, etc. and the factors K_1 and K_2 were omitted from $[R]$. The integral of $[R$ (new)$]^{\frac{1}{2}}$ was evaluated as before but divided by $(2\pi)^2$ to obtain an average. As the entropy of the rigid molecule changes by only 0.02 e.u. over the range of α this method is obviously sufficiently accurate. The symmetry number for the rigid case is unity but there is a symmetry number of three in the contribution of the methyl group. The expressions for the rotational and translational entropy and free energy were then

$$S_{t+r}=10/2\,R\ln T+11.209-\Sigma S_f-S, \qquad (4)$$

$$-\left(\frac{F^0-E_0{}^0}{T}\right)_{t+r}=10/2\,R\ln T+1.275-\Sigma\frac{F-F_f}{T}. \qquad (5)$$

The last terms in (4) and (5) are the sums of the effects of the potentials restricting the rotation of the OH and CH_3 groups (three minima in each case), which are to reduce the S and F as calculated on the basis of free rotation. They are obtained directly from Pitzer's tables.[17]

The potential hindering the rotation of the hydroxyl group to give the best fit was 10,000 cal. The results of columns three and four (Table II) were obtained using these potentials.

IV. TOTAL ENTROPY AND FREE ENERGY TABLES

The values of the total entropy and free energy are given in Table III at several temperatures on the basis of free and hindered rotation with the above potentials.

TABLE III.

		RESTRICTED ROTATION		S FROM EQUILIBRIUM DATA	
T°K	FREE ROTATION S	S	$\frac{(F^0-E_0{}^0)}{T}$	C_p's F.R.	C_p's R.R.
400	74.93	71.92	58.97	71.15	71.87
450	77.33	74.53	60.58	73.88	74.54
500	79.67	77.02	62.10	76.48	77.08
550	81.93	79.43	63.58	78.97	79.62
600	84.13	81.76	65.04	81.32	82.07

[17] Pitzer, J. Chem. Phys. **5**, 469 (1937).

V. Comparison with the Equilibrium Data

The remarkably accurate equilibrium data[18–20] for the reaction

$$C_2H_4\ (g)+H_2O\ (g)=C_2H_5OH\ (g)$$

are plotted in Fig. 1 (on the basis of fugacities). To calculate the entropy of ethyl alcohol from these data it is necessary to know the heat of reaction and the entropies of the reactants. The entropy of water vapor was obtained from the results of Gordon,[21] that of ethylene was calculated using the data and method given by Egan and Kemp.[22] In both cases the values used were from the molecular data. These are in complete agreement with experiment.[22, 23]

The heat of reaction at 25° in the standard state can be calculated to well within 400 calories from the heats of formation of the components with a correction to the ideal gas state. Table IV summarizes the calculation.

Table IV. *Heats of formation of ideal gases in calories for all P and 298.2°K.*

	Ethylene	Water	Ethyl alcohol
Liquid at 298.2	—	−68,313[24]	−66,750[25]
Vaporization at 298.2	—	10,499[26]	10,120[9]
Saturated vapor at 298.2	—	−57,814	−56,630
Real gas at 1 atmos.	12,140[27]	—	—
Berthelot correction	+12	+1	+5
Ideal gas at 1 atmos.	12,152	−57,813	−56,625
Limit of error ±	210	13	220

The correction to the ideal gas state was made on the basis of the modified Berthelot equation and the thermodynamic equation of state. It is

$$-\left[\frac{9T_cRP}{128P_c}-\frac{81}{64}\frac{RT_c^3P}{P_cT^2}\right].$$

The "I.C.T." critical constants were used in all cases.

[18] Stanley, Youell, Dymock, J. Soc. Chem. Ind. **53**, 205T (1934).
[19] Applebey, Glass, Horsley, J. Soc. Chem. Ind. **56**, 279T (1937).
[20] Dodge and Bliss, Ind. Eng. Chem. **29**, 19 (1937).
[21] Gordon, J. Chem. Phys. **2**, 65 (1934).
[22] Egan and Kemp, J. Am. Chem. Soc. **59**, 1264 (1937).
[23] Giauque and Archibald, J. Am. Chem. Soc. **59**, 561 (1937).
[24] Rossini, Nat. Bur. Stand. J. Research **6**, 1 (1931).
[25] Rossini, Nat. Bur. Stand. J. Research **13**, 189 (1934).
[26] Giauque and Stout, J. Am. Chem. Soc. **58**, 1144 (1936).
[27] Rossini and Knowlton, Nat. Bur. Stand. J. Research **19**, 339 (1937).

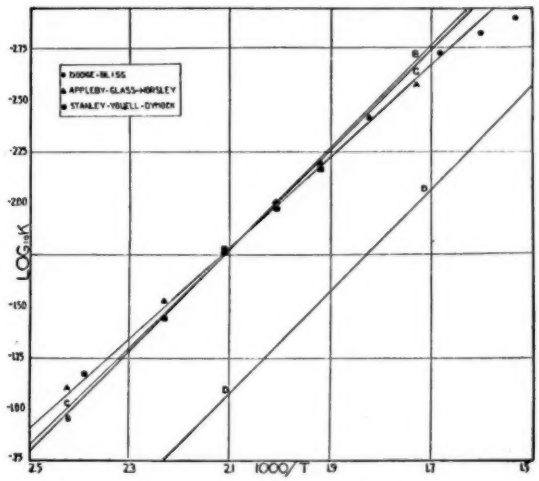

Fig. 1. Equilibrium constants for the reaction $C_2H_4(g)+H_2O(g)=C_2H_5OH(g)$.

The entropies in columns five and six of Table III were calculated from the best curve through the equilibrium data (Fig. 1). The ΔH^0 value, used to get the results in column five, was calculated from that at 25° using heat capacities obtained from the molecular data on the assumption of free rotation. For column six, heat capacities, obtained on the basis of restricted rotation with the potentials already given, were used to extrapolate $\Delta H^0_{298.2}$.

VI. Accuracy

If the frequencies δ_1, δ_2 and δ_3 are all taken at 1050, the entropy from molecular data is decreased 0.7 e.u. at 351.5°K, 0.8 e.u. at 403.2°K, and 1.3 e.u. at 600°K. The $-(F-E_0^0)/T$ value at 400 is decreased by 0.3 e.u. that at 600 by 0.5 e.u. The error in the third law entropies might be 0.3 e.u. This seems an upper limit to the error. The maximum error in $\Delta H_{298.2}$ would introduce 1 e.u. at 400°K and 0.7 e.u. at 600°K. The maximum error in ΔS from the equilibrium measurements would be the error in ΔH at 298.2 plus that in extrapolation to the temperature T. The error in the equilibrium constants themselves produces a negligible error as is evident from Fig. 1. At 400 and 600°K, respectively the limits of error due to extrapolation are 0.2 e.u. and 0.4 e.u. (i.e. if $\delta_1=\delta_2=\delta_3=1050$).

The comparison of the calorimetric entropies with those from the molecular data on the basis

of free rotation could thus be in error by 1.0 e.u. (0.7+0.3) at 351.5°K and 1.1 e.u. (0.8+0.3) at 403.2. The empirical potentials partly absorb the error in the calculation using restricting potentials.

The error in the comparison of the entropies from the equilibrium data with those from free rotation could be that in $\Delta H^0_{298.2}$ plus that in the entropy from molecular data minus that in the extrapolation of ΔH as both use the same frequencies. The maximum errors at 400°K and 600°K are thus 1.6 e.u.

The arbitrary choice of potentials for the same comparison on the basis of restricted rotation partly absorbs this error.

VII. Discussion

From the previous discussion it is at once evident that no reasonable assumption as to error can reconcile the discrepancy (about 3.0 e.u.) between the entropies calculated on the basis of free rotation and the experimental ones either from the third law or the equilibrium data. An assumption of random orientation in the crystal would reconcile the third law values, but not those from the equilibrium measurements. On the other hand, the remarkable check of the entropy values calculated with the above restricting potentials, both with the experimental results from the third law and from the equilibrium data at all temperatures, practically amounts to proof, not only of the existence of such potentials, but that the values are essentially correct (i.e., that the vibrational frequency assignment has been properly made).

The practical significance of the results is shown graphically in Fig. 1. Curve *A* is the best curve through the equilibrium data. Curve *B* represents equilibrium constants obtained from the third law data using heat capacities calculated assuming free rotation, to extrapolate above 403.2°K. The equilibrium constants plotted on curve *C* were evaluated using heat capacities, calculated on the basis of restricted rotation, to extrapolate the third law entropies and $\Delta H^0_{298.2}$. The small extrapolation is noteworthy.[28] Curve *D* was obtained using entropies from the molecular data assuming free rotation. The curve using entropies from molecular data with restricting potentials coincides with curve *C* because the potentials were solved for from the third law data at 403.2°. It is thus evident that *the thermodynamic values in Table III calculated on the basis of restricted rotation (columns 3 and 4) can be looked upon as values in best accord with all experimental facts.*

[28] Parks, Ind. Eng. Chem. **29**, 845 (1937), has also used this reaction for a third law check with a long extrapolation of which he was in doubt.

The Entropy of Acetone and Isopropyl Alcohol from Molecular Data. The Equilibrium in the Dehydrogenation of Isopropyl Alcohol

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The entropy and free energy of acetone and isopropyl alcohol gases have been calculated from the molecular data at several temperatures on the basis of (a) free internal rotation (b) restricted rotation (with the potentials: Acetone, about C−C bond=1000 cal.; isopropyl alcohol, about C−C bond=3400 cal. about C−O=5000 cal.). The va'ues based on restricted internal rotation were made to be consistent with the third law values. They are in better agreement with the ΔS values from the equilibrium data than those assuming free rotation.

I. INTRODUCTION

ANOTHER reaction which satisfies the conditions for detecting the presence of potentials hindering the rotation of groups in organic compounds[1–3] is the dehydrogenation of isopropyl alcohol to acetone

$$(CH_3)_2CHOH(g) \rightleftarrows (CH_3)_2CO(g) + H_2(g).$$

II. THE ENTROPY OF ACETONE AND ISOPROPYL FROM THERMAL DATA

Tables I and II summarize the calculation of the entropy of the hypothetically perfect gases at their normal boiling points.

III. THE ENTROPIES FROM MOLECULAR DATA

(a) Acetone

The assignment of frequencies to the twenty-two modes of vibration was made from the Raman data of Dadieu and Kohlrausch and of Trumpy.[10, 11]

Employing the principles of the previous paper[3] these are[12] C−CO−C skeleton: $\nu_1(\pi)$, 780; $\nu_1(\sigma)$, 1070; $\nu_2(\pi)$, 1715; $\delta(\pi)$, 376; $\delta_1(\sigma)$, $=\delta_2(\sigma)$, 528. CH_3 (internal): $^2\nu(\pi)$, 2950; $^4\nu(\sigma)$, 2950; $^2\delta(\pi)$, 1220; $^4\delta(\sigma)$, 1432. $(CH_3)_2>CO$ (hydrogen angle variation): $\delta_1=\delta_2=\delta_3=\delta_4$, (880) (calc. free rotation): (950) (calc. restricted rotation). The average value of 880 cm^{-1} for last four frequencies δ_i which are similar to the $\nu_\alpha M$ frequencies in ethane was obtained from the gaseous heat capacity measurements,[13, 14] as discussed elsewhere[1, 15] on the assumption of free internal rotation. The value 950 cm^{-1} was obtained similarly on the basis of restricted rotation of methyl

TABLE I. *The calorimetric entropy of acetone at 329.3°K.*

	E.U./MOLE
0°K (cryst.)–298.16°K (liquid)[4]	47.9 ±.3
Liquid 298.16–329.3[5]	3.10±.05
Vaporization 7090/329.3[6]	21.53±.1
Entropy of actual gas at boiling point (329.3°K)	72.53±.5
Correction for gas imperfection[7]	.13
Entropy of ideal gas at boiling point	72.7 ±.5

TABLE II. *The calorimetric entropy of isopropyl alcohol at 355.5°K.*

	E.U./MOLE
0°K (cryst.)–298.16°K (liquid)[4]	43.0 ±.3
Liquid 298.16–355.5[8]	8.07±.2
Vaporization $\frac{(161.7+159.2)}{2\times355.5}$ 60.09[6, 9]	27.12±.2
Entropy of actual gas at boiling point (355.5°K)	78.19±.7
Correction for gas imperfection[7]	.09
Entropy of ideal gas at boiling point	78.3 ±.7

[1] Kemp and Pitzer, J. Am. Chem. Soc. **59**, 276 (1937).
[2] Pitzer, J. Chem. Phys. **5**, 469, 473 (1937).
[3] Schumann and Aston, J. Chem. Phys. (See previous paper.)
[4] Kelley, J. Am. Chem. Soc. **51**, 1145 (1929).
[5] Williams and Daniels, J. Am. Chem. Soc. **47**, 1490 (1925).
[6] Matthews, J. Am. Chem. Soc. **48**, 562 (1926).
[7] From thermodynamics and the modified Berthelot equation—

Acetone	$P_c=47$ atmos.	$T_c=508$°K. I.C.T.
Isopropyl Alcohol	$P_c=53$ atmos.	$T_c=508$°K. I.C.T.

[8] Williams and Daniels, J. Am. Chem. Soc. **46**, 903 (1924).
[9] Parks and Nelson, J. Phys. Chem. **32**, 61 (1928).
[10] Dadieu and Kohlrausch, Monat **55**, 201 (1930).
[11] Trumpy, Kgl. Norske Videnskap Selskabs Skrifter No. 9, 1–20 (1935).
[12] C−CO−C skeleton frequencies were assigned by comparison with formaldehyde. The ∂_2 frequency is predominantly CO stretching. The results of Duncan for the excited electronic states confirm this assignment. Duncan, J. Chem. Phys. **3**, 384 (1935).
[13] Wiedmann, Wied. Ann. **2**, 195 (1877).
[14] Regnault, Mem. de l'Acad. **26**, 1 (1862).
[15] See also Aston, Siller and Messerly, J. Am. Chem. Soc. **59**, 1743 (1937).

groups with the potentials found later. As will be evident presently, a method of successive approximations had to be used. The values obtained on the basis of restricted rotation are close to the average value for these vibrations in ethane (920 cm^{-1}). The vibrational entropy and free energy were calculated on the basis of these frequencies from Nernst's tables.

The rotational entropy and free energy were calculated on the basis of free rotation[3] using the distances: CH = 1.11A; CC = 1.54A CO = 1.24A[16] <CCC 109° 28′ (CCOC skeleton planar).

With the <CCC lying in the x, y plane, the y axis bisected this angle. The diagonal terms of the matrix of moment of inertia[17] using parallel axes through the center of gravity times 10^{40} are in order

$$83.9, \quad 90.6, \quad 174.5, \quad 5.46, \quad 5.46.$$

As the rest of the terms are zero these are reduced moments about the principal axes. The symmetry number is 18. The entropy and free energy due to rotation and translation are given, respectively, by

$$S_{t+r} = 10/2R \ln T + 11.545, \tag{1}$$

$$-((F - E_0')/T)_{t+r} = 10/2R \ln T + 1.611. \tag{2}$$

Table III (column 1) summarizes the calculations of the total entropy at the normal boiling

TABLE III. *The entropy of acetone from molecular data.*

	329.3°K FREE ROTATION	329.3°K RESTRICTED ROTATION
$S_{t,r}$	69.14	69.14
S_{vib}	4.15	3.99
$2(S_f - S)(CH_3, 1000$ cal.)	—	.48
Entropy of the ideal gas	73.29	72.65
Discrepancy	.6	—

point from molecular data on the basis of free rotation.

The discrepancy of 0.6 entropy units between this result and that from the thermal data (Table I) is almost within the experimental error. However, a better fit can be obtained on the basis that a potential of 1000 calories restricts the internal rotation of each methyl group. Table III (column 2) summarizes the calculation on this basis. For such small potentials no great error has been found to result if the restricting terms are subtracted directly from the values for free rotation,[2] and this procedure has been followed for acetone.

TABLE IV. *The entropy of isopropyl alcohol from molecular data.*

	355.5°K FREE ROTATION	355.5°K RESTRICTED ROTATION
$S_{t,r}$	76.17	64.10
S_{vib}	6.35	6.15
$2S_{rr}(CH_3, 3400$ cal.)	—	4.96
$S_{rr}(OH, 5000$ cal.)	—	3.07
Entropy of the ideal gas	82.52	78.28
Discrepancy	4.2	—

(b) Isopropyl alcohol

The frequencies of isopropyl alcohol can be assigned by analogy with the spectra of ethyl alcohol and acetone. Using the Raman data of Dadieu, Pongratz, and Kohlrausch[18]

C−CO−C skeleton: $\nu_2(\pi)$, 815; $\nu_1(\pi)$, 875; $\nu_1(\sigma)$, 940; $\delta(\pi)$, 370; $\delta_1(\sigma)$, 420; $\delta_2(\sigma)$, 490.
CH_3 (internal): $^2\nu(\pi)$, 2870; $^4\nu(\sigma)$, 2920; $^2\delta(\pi)$, 1340; $^4\delta(\sigma)$, 1450.
OH (internal): ν, 3300.
CH (secondary) (internal): ν, 2900.
C−O−H (hydrogen angle variation): δ_7, (700).
$(CH_3)_2$>CH−O (hydrogen angle variation): $\delta_1 = \delta_2 = \delta_3 = \delta_4$, (880) (free rotation): (950) (restricted rotation); $\delta_5 = \delta_6$, 1105.

The frequencies $\delta_1 = \delta_2 = \delta_3 = \delta_4$ have been taken to be the same as the corresponding ones in acetone. δ_7 has been assigned the value for the analogous vibration in methyl alcohol. The assignment of 1105 cm^{-1} to $\delta_5 = \delta_6$ which are taken as due to angular motion of the CH group, is uncertain, but can produce no great error, as will be shown presently.

The rotational contributions were evaluated employing the same method and interatomic constants used previously for ethyl alcohol.[3] With axes along the same directions relative to the C−C−C grouping as were used for acetone,

[16] Brockway, Rev. Mod. Phys. **8**, 231 (1936).
CH_3CHO; CO = 1.20A Cl_2CO; CO = 1.28A.

[17] Kassel, J. Chem. Phys. **4**, 276 (1936).

[18] Dadieu, Pongratz, Kohlrausch, Monat. **61**, 369 (1932)

TABLE V.

T°K	Free Rotation ΔS	Restricted Rotation ΔS	ΔS Equilibrium Data	
			C_p's F.R.	C_p's R.R.
355.5	24.69	28.28	—	—
400	25.08	28.39	—	—
450	25.41	28.44	27.89	27.37
500	25.61	28.35	28.26	27.52

the terms of Eq. (1) of the previous paper[3] times 10^{40} are:

$$(xx)=88.69-1.95\sin\alpha+1.28\sin^2\alpha,$$
$$(yy)=61.51+2.84\cos\alpha+0.86\cos^2\alpha,$$
$$(zz)=34.85-2.21\cos\alpha+0.42\cos^2\alpha,$$
$$(xy)=1.03\sin\alpha+1.05\sin\alpha\cos\alpha,$$
$$(xz)=1.46\sin\alpha+0.74\sin\alpha\cos\alpha,$$
$$(yz)=-32.59-0.13\cos\alpha+0.60\cos^2\alpha.$$

(where α orients the OH group)

$$(\lambda\lambda)=7.29,\ (\mu\mu)=4.07,\ (\nu\nu)=0.89,$$
$$(\lambda\mu)=0,\ (\lambda\nu)=0,\ (\mu\nu)=-0.63,$$
$$K_{OH}=1.32,\quad K_{CH_3}=5.46,$$
$$\sigma=9.$$

The determinant is again a function of the angular position of the asymmetrical OH top. Assuming free rotation, the translational and rotational entropy and free energy are found to be:

$$S_{t+r}=11/2R\ln T+12.235 \quad (3)$$

$$-((F^0-E_0^0)/T)_{t+r}=11/2R\ln T+1.307. \quad (4)$$

Table IV, column 1, summarizes the calculation of the entropy of isopropyl alcohol from the molecular data, assuming free rotation. The discrepancy from the thermal data of Table II can be explained by a potential of 3400 calories restricting the rotation of methyl groups and a barrier of 5000 calories hindering hydroxyl rotation. Table IV, column 2, summarizes the calculation at the normal boiling point using these potentials. In evaluating the rotational contributions for the rigid molecule, $[R_{\text{rigid}}]^{\frac{1}{3}}$ was averaged over all positions of the hydroxyl group. The calculation was thus similar to that for ethyl alcohol.[3] The symmetry number was taken to be unity for this part of the rotational entropy. In the calculation of the contribution of each hindered methyl group to the rotational entropy, the symmetry number is, of course, three. Thus utilizing the above potentials, Eqs. (3) and (4) are replaced by (5) and (6)

$$S_{t+r}=11/2\ R\ln T+12.020-\Sigma(S_f-S), \quad (5)$$

$$-\left(\frac{F^0-E_0^0}{T}\right)_{t+r}=11/2\ R\ln T+1.092-\Sigma\left(\frac{F-F_f}{T}\right). \quad (6)$$

IV. Comparison with the Equilibrium Data

Parks and Kelley[19] have obtained equilibrium data for the reaction,

$$(CH_3)_2\,CHOH\ (g)\rightleftarrows(CH_3)_2\,CO\ (g)+H_2\ (g),$$

which are consistent to about 8 percent in K. The heat of this reaction has recently been measured at 355°K[20] with an accuracy of 100 cal./mole. Table V summarizes the ΔS values, calculated from these data for the reaction as written above, and compares them with the values determined from molecular data both for free and restricted rotation, using the known entropy of hydrogen gas.[21, 22]

Column 2, Table V gives the results, at several temperatures, of the calculations from the molecular data, assuming free rotation. Column 3 lists results obtained on the basis of potential barriers, of the values determined above, restricting the rotation of methyl and hydroxyl groups. Column 4 lists values of ΔS calculated from the best straight line through the equilibrium data, using values of ΔH° extrapolated to

TABLE VI.

°K	Restricted Rotation Acetone $S-\left(\frac{F^0-E_0^0}{T}\right)$		Restricted Rotation Isopropyl Alcohol $S-\left(\frac{F^0-E_0^0}{T}\right)$	
355.5	74.15	60.08	78.29	62.73
400	76.73	61.77	81.61	64.68
450	79.58	63.55	85.23	66.78
500	82.23	65.28	88.71	68.81

[19] Parks and Kelley, J. Phys. Chem. **32**, 734 (1928).
[20] We wish to thank Professor G. B. Kistiakowsky for giving us this result prior to publication. Dolliver, Gresham, Kistiakowsky, Smith, Vaughan, J. Am. Chem. Soc. **60**, 440 (1938).
[21] Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).
[22] Davis and Johnston, J. Am. Chem. Soc. **56**, 1045 (1934).

the desired temperature assuming free rotational heat capacities. The values in column 5 were calculated with ΔH° values extrapolated with the aid of heat capacities on the basis of restricted rotation. For completeness, the entropy and free energy of acetone and isopropyl alcohol is tabulated in Table VI from 355.5°K to 500°K on the basis of restricted rotation.

V. Accuracy

The assignment of the δ_i frequencies in both acetone and isopropyl alcohol may cause an error of as much as 0.5 e.u. at 355°K and 0.8 e.u. at 500°K in the entropy of each compound. This error will largely cancel in the calculation of ΔS and in the extrapolation of ΔH. Neglecting the negligible error in the equilibrium constants themselves, the error in ΔS from the equilibrium measurements is that in ΔH_{355} plus that due to extrapolation. The total could hardly exceed 0.5 e.u. at 500°K.

The uncertainty in the calorimetric entropies of the gases is large. The comparison of the ΔS, based on restricting potentials determined calorimetrically, with that from the equilibrium data might be in error by as much as 2 e.u. at 500°K. Such an error is of course improbable. That the potentials solved for are of the expected order of magnitude is an indication of a much smaller error.

The comparison of the ΔS from the equilibrium data with that from the molecular data assuming free rotation could not be in error by more than 1 e.u. at 500°K and 0.7 e.u. at 355°K.

VI. Discussion

It is apparent, in the case of isopropyl alcohol, that no assumption of error can explain the discrepancy of 4.2 e.u. between the third law entropy and that calculated assuming free rotation. Potential barriers hindering rotation, of the same order of magnitude found for other compounds, will account for the discrepancy. The high symmetry of the acetone molecule would suggest relatively free rotation about C−C bonds: that the discrepancy in this case is only 0.6 e.u. tends to confirm this. No hypothesis based on random orientation in the crystal can square the results calculated on the basis of free rotation with those from the equilibrium measurements.

In view of the relatively high limit of error of these calculations, the check assuming restricted rotation is but a probable one. However the mass of accumulated evidence in favor of restricted rotation with potentials greater than 3000 calories[2, 3, 23, 24] leaves practically no doubt that this cause explains the lack of agreement of experimental third law entropies with these calculated on the basis of free rotation.

[23] Howard, J. Chem. Phys. **5**, 451 (1937).
[24] Kistiakowsky and Nazmi, J. Chem. Phys. **6**, 18 (1938).

The Role of Free Radicals in Elementary Organic Reactions

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The primary reactions between radicals and organic molecules are discussed from the point of view of a principle which states that there shall be least change in atomic position and least change in electronic configuration during an elementary reaction. We have concluded that alkyl radicals will attack most easily exposed positive atoms, i.e., in organic molecules, the hydrogen atoms. The attack on exposed negative atoms such as N, O or Cl is less probable whereas a completely shielded carbon atom should certainly not be attacked in the primary step. A doubly or triply bonded carbon atom can, however, react with a radical. These statements are discussed from the experimental point of view, together with the question as to when it is necessary to assume that organic reactions proceed through radical chains.

1. INTRODUCTION

ONE of the questions in connection with the thermal decomposition of organic compounds is whether the product molecules are formed in a single elementary act or through some sort of radical chain mechanism or whether both processes occur simultaneously to an appreciable extent. If we assume a radical mechanism, there are a great many more possibilities than with a non-radical mechanism and this leads to one evident objection: we know so little about radicals that we might postulate any sort of reaction and thereby could attribute any effect to them. However, our experience is not altogether so small and we can learn something about them from chemical physics and compare the results with the chemical behavior.

In this paper we shall try to consider how our chemical experience with organic molecules and free radicals can be summed up in terms of shielding effects and effects connected with the electronic structures of the reacting particles. The views expressed, however, are not intended to be definite statements of how molecules and radicals react; it is our intention to consider how strongly we can restrict the properties of radicals and to discuss some of the various possible reaction schemes, emphasizing those that are not in disagreement with organic experience and with chemical physics.[1]

[1] We have not attempted a quantitative treatment of these problems such as that of Eyring and Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931). The practical application of such calculations seems to us to be valuable only insofar as they suggest qualitative ideas. To draw quantitative conclusions from them is extremely difficult because the approximations which must be made in order to make the calculations feasible are of the same order of magnitude as the quantities calculated.

2. PRINCIPLE OF LEAST MOTION [2]

It is most desirable that the activation energy necessary to bring the atoms from the old to the new positions be as small as possible and, in general, this is fulfilled if there be as little motion as possible in passing from the old to the new configuration. The principle of least motion is a statement of certain conditions that favor a low activation energy and this principle will be discussed from the standpoint of least motion of (*a*) the atoms and (*b*) the electronic configuration of the reacting system. From both these standpoints it is plausible to assume that in general the activation energy of an elementary reaction will be smaller if not many bonds have to be broken.

(a) From the first standpoint, in order for maximum gain of resonance energy to occur, it is necessary for the atoms of the system to move through a considerable fraction (approximately half) of the distance towards the configuration which they will have after the new bond forms.

[2] Statements very similar to that which we call the principle of least motion have been proposed by Franck and Rabinowitch, Zeits. f. Elektrochem. **36**, 794 (1930). Calculations of Eyring and collaborators, J. Am. Chem. Soc. **54**, 2661, 3876 (1932) on the reaction complexes also contain this principle in an implicit form.

The energy necessary to do this can be estimated from the known vibrations of the original molecules together with the contribution of the van der Waals energy. In this connection we note that it takes about four or five times more energy to make a displacement along the direction of a bond, stretching the bond thereby, then to make the same displacement perpendicular to the direction of the bond, merely changing the valence angle; and that as the nuclei move further from their equilibrium positions the energy required becomes greater with displacements according to a quadratic law. Thus it is most desirable that there should be little change of the position of atoms and in particular little change in the valence distance while passing from the old to the new configuration.

(b) From the second standpoint, if the atoms have assumed a configuration similar to the one where the new bonds can be written, i.e., to a point about halfway between the initial and final configuration, the electronic configuration becomes important; if the electron orbits do not have to change much in order to get from the old to the new valence picture we will have a strong resonance and a lowered activation energy.

The principle of least motion is illustrated in Fig. 1. The abscissae correspond to atomic configurations, point *A* being the configuration before and point *B* the configuration after the reaction. The ordinates show the potential energies corresponding to each atomic configuration. Curve I represents the potential energies to be expected if the bonds (electron orbits) remain as they have been in the original configuration *A*. Curve II shows the potential for the bonds arranged as they are in the final state *B*.

At the crossing point *C* the same energy will correspond to two different electronic configurations. This resonance will lower the energy as is shown in Fig. 1 by the dotted curve. Thus we may expect a low activation energy if (a) the distance *AC* is small (principle of least motion of the atoms), if (b) the lowering of the energy by resonance is great; one necessary condition for the latter is that the spacial distribution of the electrons for the two resonating valence systems should not be very different (principle of least motion of the electronic configuration).

3. Reactions of Radicals with Positive Atoms

A reaction of this type in which a univalent radical R reacts with a hydrocarbon such as ethane is,

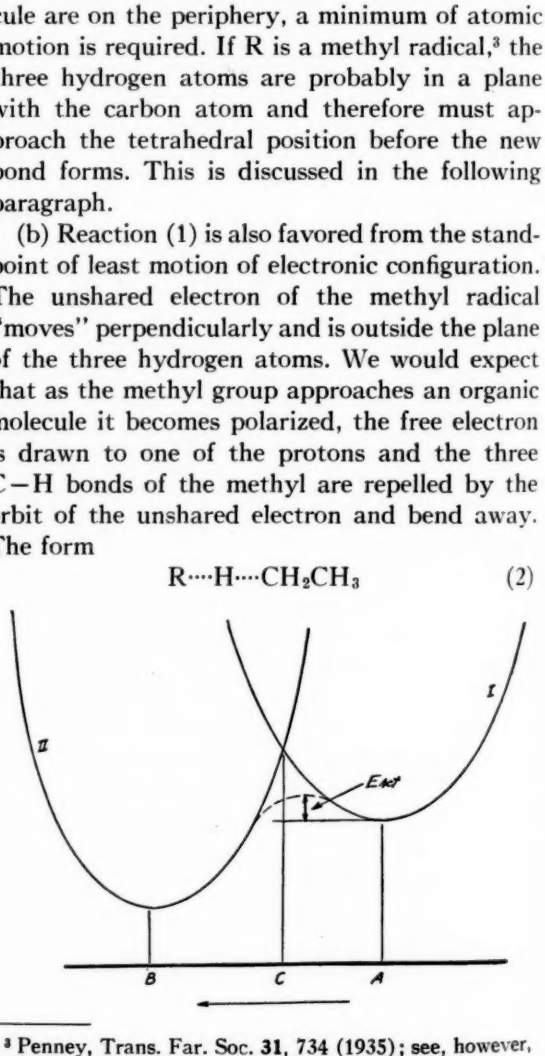
$$R+C_2H_6\rightarrow RH+CH_3CH_2. \qquad (1)$$

The radicals which most commonly come into question according to chemical experience are methyl and ethyl groups or hydrogen atoms; larger radicals are very unstable and in any case would behave in the same way.

(a) From the standpoint of least motion of the atoms everything is in favor of reaction (1). Inasmuch as the positive atoms of an organic molecule are on the periphery, a minimum of atomic motion is required. If R is a methyl radical,[3] the three hydrogen atoms are probably in a plane with the carbon atom and therefore must approach the tetrahedral position before the new bond forms. This is discussed in the following paragraph.

(b) Reaction (1) is also favored from the standpoint of least motion of electronic configuration. The unshared electron of the methyl radical "moves" perpendicularly and is outside the plane of the three hydrogen atoms. We would expect that as the methyl group approaches an organic molecule it becomes polarized, the free electron is drawn to one of the protons and the three C−H bonds of the methyl are repelled by the orbit of the unshared electron and bend away. The form

$$R\cdots H\cdots CH_2CH_3 \qquad (2)$$



[3] Penney, Trans. Far. Soc. **31**, 734 (1935); see, however, Nordheim-Pöschl, Ann. der Physik **26**, 258 (1936).

intermediate between the two forms in reaction (1) can therefore probably be formed with a relatively low activation energy.

Another type of reaction of a radical with a positive atom is illustrated by the equation

$$-CH_2CH_3+C_2H_6\rightarrow CH_2{:::}C\cdots H\cdots H\cdots CCH_3 \quad (H,H) \rightarrow CH_2=CH_2+H_2+-CH_2CH_3. \quad (3)$$

In this case not only are two bonds broken but also saturated parts of the compounds get into contact with each other preceding the reaction; it seems probable from both the (a) and (b) standpoints that the simpler reaction (1) will have a lower activation energy.

4. Reactions of Radicals with Exposed Negative Groups

Examples of this type of reaction are given by ethers, amines and halogen compounds.

$$R+CH_3OCH_3\rightarrow CH_3OR+CH_3, \quad (4)$$

$$R+CH_3NH_2\rightarrow RNH_2+CH_3, \quad (5)$$

$$R+CH_3Cl\rightarrow RCl+CH_3. \quad (6)$$

(a) Since there is very little shielding effect in any such reactions we can say, from the standpoint of least motion of the atoms, that there may always be attack on exposed negative atoms.

(b) We should expect that the resonance factor would be less favored in reactions (4), (5), and (6) than in reaction (1) because of the following reason: The negative atom (O, N or Cl) repels the unshared radical electron; on the other hand because of the partially polar nature of the bond to be formed, the radical electron will be shifted in the reaction product towards the negative group. Thus the radical electron has widely differing positions at the beginning and the end of the reaction. Although, according to this consideration, the principle of least motion of the electrons does not favor the attack of radicals on negative groups we do not think that on the basis of this reasoning alone we can definitely exclude such reactions. Also from the experimental point of view this type of reaction has not been excluded definitely since even if the exposed negative groups would be attacked by methyl radicals, this could not be noticed unless the reaction complex splits off a radical different from the original one.

The attack of a radical on, for example, *n*-propylamine may be represented as first forming an intermediate complex,

$$CH_3CH_2CH_2N(H_2)+CH_3\rightarrow \left[\begin{matrix}CH_3CH_2CH_2NCH_3\\ H_2\end{matrix}\right]^+_-, \quad (7)$$

in which the positive ion $\left[\begin{matrix}CH_3CH_2CH_2NCH_3\\ H_2\end{matrix}\right]^+$ is combined with an electron moving in an outer orbit instead of with a negative ion. The tendency of the negative atom to push away the radical electron will in this case produce an electron configuration approaching that of the final product. The reaction product in (7) has an ionic nature but there is probably no actual dissociation so that it would not be possible to prove its existence experimentally by testing for free electrons; the ionic form in (7) may, however, decompose into a free radical and a molecule differing from those out of which it was built up so that an experimental test could be made by adding methyl radicals to higher amines. Another experimental test would be to look for absorption in the visible or near ultraviolet during the reaction since the loosely bound electron would probably give rise to absorption of relatively long wave-length; however, such experiments do not permit one to distinguish between the different possible kinds of attack on the negative group. A reaction of type (7) could also occur with organic oxygen compounds with formation of oxonium compounds but this is presumably much less likely than with nitrogen.

The somewhat inadequate experimental evidence available indicates that free radicals do not react to an appreciable extent with exposed negative groups. The decomposition of *n*-propylamine appears to proceed through a chain reaction [4] but a careful examination of the products of the partially decomposed material indicated the absence of lower amines.[5] Also methyl ethyl ether was decomposed by the introduction of methyl radicals and dimethyl ether was found to be

[4] Sickman and O. K. Rice, J. Am. Chem. Soc. **57**, 22 (1935).

[5] Unpublished work by F. O. Rice and P. M. Ruoff.

absent [6] from the products proving that the reaction,

$$CH_3+CH_3OCH_2CH_3\rightarrow CH_3OCH_3+CH_3CH_2 \quad (8)$$

did not occur to an appreciable extent. The experimental results with *n*-propylamine and methyl ethyl ether indicate that if there is any formation of ammonium or oxonium ions, it is followed by redissociation into the original parts.

5. Reactions of Radicals with Shielded Negative Groups

An example of this type of reaction is,

$$R+CH_3CH_3\rightarrow R-CH_3+CH_3. \quad (9)$$

(a) From the standpoint of least motion of the atoms, there seems to be an insuperable objection to any reaction similar to Eq. (9), even in the case where R is a hydrogen atom. The shielding effect of the hydrogen atoms or other groups surrounding the carbon atom that is being attacked is so powerful that it seems extremely improbable that a radical can combine with a carbon atom in a paraffin hydrocarbon.

In order to obtain an estimate of this shielding effect, we will consider the exchange reaction between a hydrogen atom and methane. We will calculate the energy required to push three of the C−H bonds of methane into a plane since we may assume that at least this amount of motion of the three hydrogen atoms must occur before the new bond can form. This we will do in two steps which we do not consider as taking place in succession but actually simultaneously. Our reason for separating the process into these two steps is that in this way we can deal in the first step with those effects for which a fair estimate is possible. This first step will consist in pushing the three C−H bonds of methane into the same plane with the carbon in order to make room for the new substituent which we shall add in the second step.

Methane has four proper vibrations but only in one, namely in that of 1304 wave numbers do the atoms move strongly towards the configuration where three hydrogen atoms lie in the same plane with the carbon. In this vibration, the C−H distances remain approximately constant but the valence angles change considerably. We shall make two approximations, (1) that the mass of the carbon is infinite and (2) that the three hydrogen atoms move in a direction parallel to the line joining the fourth hydrogen to the carbon; this involves errors of about ±10 percent. The anharmonicity of the forces during this fairly large displacement has also been neglected.

Combining the equation for the relation between the frequency and mass of the hydrogen atom,

$$\nu=\frac{1}{2\pi}\left(\frac{k}{m}\right)^{\frac{1}{2}}$$

with the equation for its potential energy as a function of distance,

$$E=\tfrac{1}{2}kx^2$$

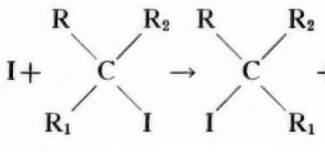
and remembering that there are three hydrogen atoms, we obtain

$$3E=6\pi^2m\nu^2x^2.$$

The value of x is $1.09\times\frac{1}{3}=0.36$A and after making the other substitution we obtain $3E=40$ Cal. per mole which is the energy required to push the three hydrogen atoms into a plane. After the methane molecule has been distorted, a hydrogen atom is brought into position at the antipole of the fourth hydrogen atom of the original molecule and the fourth hydrogen atom itself is then expelled; this is analogous to the well-known hydrogen exchange reaction, $H+H_2\rightarrow H_2+H$. We should not expect therefore any very strong attraction between the distorted CH_4 and the oncoming hydrogen atom; indeed even a slight repulsion is more probable. Thus the whole reaction will probably not have a much lower activation energy than 40 kcal., whereas the measured activation energy for

$$H+CH_4\rightarrow H_2+CH_3 \quad (10)$$

is less than 20 kcal. It should however be mentioned in this connection that the similar reactions



(10′)

[6] Unpublished work by F. O. Rice and W. D. Walters.

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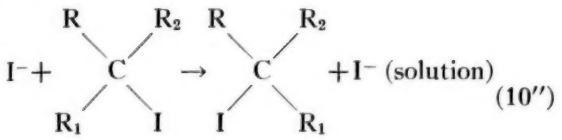


(10″)

seem to proceed[7] with activation energies in the range 14–18 kcal. However it is not impossible that the first of these reactions is really more complicated, taking place actually on the walls whereas in the second case, the attraction between the iodine ion and the substrate molecule may appreciably lower the actual activation energy that is needed.

(b) From the standpoint of least motion of the electrons, the arguments that might be used are similar to those given in Section 4 (b) for the attack of a free radical on *exposed* negative groups. However such arguments are less valid here because carbon is only slightly negative; moreover the principle of least motion of the atoms excludes the reaction so definitely that it seems unnecessary to discuss the question from the standpoint of electronic structure.

6. Reactions of Radicals with Unsaturated Compounds

Examples of this type of reaction are found in the great variety of polymerization reactions that occur. For example, when methyl radicals are produced in the presence of ethylene,[8] a reaction occurs as follows,

$$CH_3+CH_2=CH_2\rightarrow CH_3CH_2CH_2 \qquad (11)$$

and this building up process continues until the large radicals combine or disproportionate. The effect is shown by many unsaturated hydrocarbons but not by paraffin hydrocarbons; it also occurs with formaldehyde but not with acetaldehyde or acetone.[9]

(a) From the standpoint of least motion of the atoms, it is clear that the shielding effect of the hydrogen atoms is not present to the same degree as in paraffin hydrocarbons and the situation so far as atomic motion is concerned is somewhat analogous to the reactions with exposed negative groups discussed in Section 4. However substitution of the hydrogen atoms in ethylene, by radicals, should increase the difficulty of reaction and it has been found experimentally [10] that the rate of polymerization of propylene $CH_3CH=CH_2$ by methyl radicals is only about one-tenth the rate of ethylene. Similarly the substitution of one or two hydrogen atoms in formaldehyde by methyl groups to give acetaldehyde and acetone, respectively, greatly diminishes the tendency to polymerize.

(b) From the standpoint of formation of a homopolar bond, the first action is in a slightly unfavorable sense because the approach of the methyl or other radical to the dense electron cloud surrounding the doubly bound carbon atoms, induces a dipole in the radical and its free electron is repelled; this effect, however, is not as unfavorable as the similar one in the case of exposed negative groups. The induced dipole is smaller and the final product is homopolar so that the difference in electron position at the beginning and end of the reaction will be here appreciably less than for the negative groups. This same contrast between the behavior of a double bond and a negative group may also be brought out in the following way. A bond such as N–R, O–R or Cl–R can be formed only by the radical donating an electron, that is reducing the negative atom; this as we have seen meets with difficulties. In case of attack on a double bond, the alternative possibility exists, namely that the methyl group can draw out an electron from the double bond. This will depend on the electron affinity of the methyl group; it is certainly less oxidizing than chlorine and could not therefore draw an electron from chlorine; however, the fact that double and triple bonds are readily oxidized suggests that the methyl radical may be in this case regarded as analogous to an oxidizing agent and can accept an electron from the double bond. The widely spread electronic structure of the double bond and its high polarizability would aid this possibility. Of course this process

[7] Bergmann, Polanyi and Szabo, Zeits. f. physik Chemie **20B**, 161 (1933); Ogg and Polanyi, Trans. Far. Soc. **31**, 482 (1935).

[8] Taylor, Proc. Am. Phil. Soc. **65**, 90 (1926); Taylor and Jones, J. Am. Chem. Soc. **52**, 1111 (1930).

[9] Sickman and Allen, J. Am. Chem. Soc. **56**, 1251 (1934); see, however, Blacet and Volman, J. Am. Chem. Soc. **60**, 1243 (1938). Leermakers, J. Am. Chem. Soc. **56**, 1899 (1934).

[10] Private communication from Dr. D. V. Sickman.

of oxidizing the double bond should not be taken too literally since the bond to be formed is homopolar; the electron to be drawn out from the double bond will get only to about half the distance between the two groups so that one cannot say whether the radical or the double bond is really oxidized.

Another difference between the attack on negative groups and the addition reactions is that in the latter energy is liberated during the addition, whereas in the former the energy change during the reaction is negligible. It will be seen from Fig. 1 that if in the reaction, energy is gained (i.e., if point B is lower than point A) then the activation energy for the reaction (starting from A) will be lowered.

These factors will tend to make the activation energy for the addition reactions smaller than the activation energy for the attack on negative groups.

7. Decomposition of Small Organic Molecules

It is convenient to consider first the decomposition of smaller molecules of not more than four or five atoms in a chain. The following equations represent the chemical course of the reactions for some typical smaller organic molecules; the measured activation energies for the over-all reactions are also included.

$$C_2H_6 \rightarrow CH_2=CH_2+H_2 \qquad E=73{,}200 \text{ kcal.} \qquad (12)$$

$$CH_3OCH_3 \rightarrow CH_4+HCHO \qquad E=58{,}500 \text{ kcal.} \qquad (13)$$

$$CH_3COCH_3 \rightarrow CH_4+CH_2=CO \qquad E=68{,}500 \text{ kcal.} \qquad (14)$$

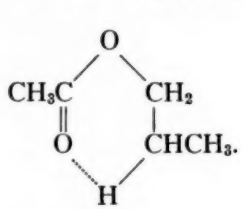
$$CH_3CHO \rightarrow CH_4+CO \qquad E=45{,}500 \text{ kcal.} \qquad (15)$$

Considering first reactions (13), (14) and (15), the direct molecular decomposition may proceed in one of two ways: either a C−H bond is broken first, the hydrogen atom migrates through a rather long distance to another part of the molecule and reacts there with a shielded carbon atom (according to our previous considerations it is highly unlikely that this could happen with the activation energies found experimentally which in the first place would have to exceed the energy of the C−H bond); or one may assume that a C−O−bond in (13) or a C−C bond in (14) and (15) is broken first and that the radicals formed in that way rotate and recombine. In this case the expected activation energies would not be much greater than those found; however once the radicals are formed, the chain mechanism seems to be the more likely one.

The decomposition of ethane according to Eq. (12) is by no means so unlikely as the reactions represented in (13), (14) and (15). Although two C−H bonds have to be broken, the energy of an H−H bond and the energy difference between a double and a single bond may be gained without moving the atoms through very large distances. Even so we believe that the radical mechanism is the more probable alternative.

8. Decomposition of Chelate Compounds

In those cases of large organic molecules with exposed negative groups or with double or triple bonds, the principle of least motion of the atoms suggests the possibility of a direct intramolecular decomposition into product molecules. The pyrogenic decomposition of esters and acetals has been studied experimentally [11] and the possibility has been considered of the ester decomposition proceeding through an intracyclic compound. This may be illustrated for n-propyl acetate by the equation,



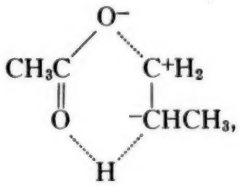
(16)

For this type of decomposition to occur, the radical R′ in an ester R COOR′, must have at least two carbon atoms and also a chemical structure such that a substituted ethylene or other molecule can split off.

Equation (16) seems however to meet an objection from the point of view of least motion of electrons, since in this case also the electron of the hydrogen atom will be repelled while approaching the oxygen atom of the carbonyl

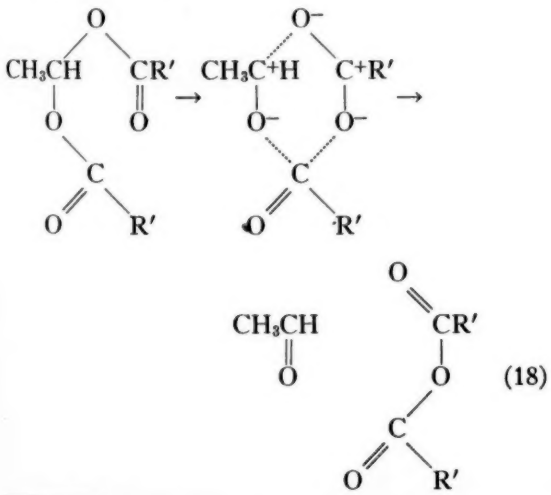
[11] Sielisch & Grund, *Uber den Mechanismus intra-und intermoleculare Reaction*, (Verlag Walters Blank, Berlin, 1932); Bilger and Hibbert, J. Am. Chem. Soc. **58**, 823 (1936). See in this connection, Kassel, J. Chem. Phys. **1**, 749 (1933); O. K. Rice and Gershinowitz, ibid., **3**, 486 (1935).

group and thus the formation of a homopolar bond will be made more difficult. On the other hand the reaction is helped on by the fact that the initial state is in resonance with the electron configuration



(17)

which provides an intermediate step to the electron configuration of the final product. The broken valence bonds may be regarded as purely electrostatic. The same sort of reasoning may be applied to other similar reactions (Eqs. (18) to (22)). We may expect therefore that the direct decomposition of esters into product molecules will occur to a greater or less extent even to the almost complete exclusion of the radical chain process.[12] Indeed this appears to be the case for the thermal decomposition of esters of the general formula $(R'COO)_2CHR$ which decompose homogeneously in the gaseous state giving an aldehyde and an acid anhydride.[13] These esters decompose at a measurable rate in the temperature range 200–300°C and have an activation energy of approximately 33,000 Cal. The decomposition may be represented as follows:



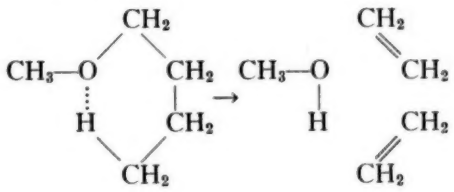
(18)

[12] See in this connection Hurd and Blunck, Abstract read at Chapel Hill meeting Am. Chem. Soc., April, 1937; Hurd, Seventh Organic Symposium, 1937.

[13] Coffin, Can. J. Research **5**, 636 (1931); idem., Trans. Roy. Soc. Can., Section III, **27**, 161 (1933); Dacey and Coffin, Can. J. Research, **15**, 260 (1937).

Indeed this reaction proceeds more easily than any other mentioned in this group. In this case, from the point of view of electronic structure, the first action is in a favorable sense; the positive carbon atom attracts the electron of the neighboring negative oxygen. Also in the intermediate structure all the negative ions are oxygen ions which will form more easily than the negative carbon ions used in (17).

Many other decompositions of this type may be given and a few examples are shown in the following equations:



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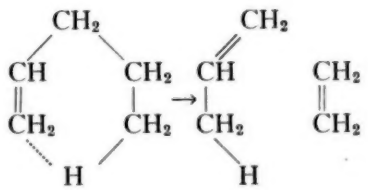
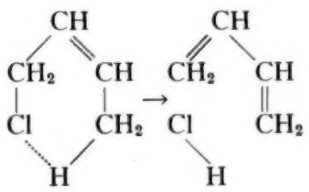


(20)



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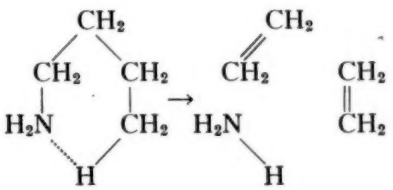


(22)

Such thermal decompositions have not been studied very extensively, and not very much is known concerning them.

However, there is more evidence on the photochemical decomposition of higher ketones and aldehydes. Since light acts primarily on the electrons, the principle of least motion of the atoms must be upheld for the primary photochemical process; indeed it becomes in this case identical with the Franck-Condon principle stating that during light absorption, the position of the heavy

particles should not change. This rule holds for the primary photochemical process much more strictly than the principle of least motion of atoms in thermal decompositions. On the other hand, light absorption may change the electronic configuration essentially, and thus invalidate the principle of least motion of electrons.

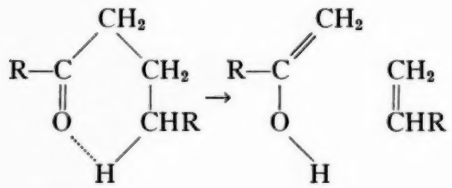
The over-all equations for the photochemical decomposition of the following three ketones may be represented as follows:[14]

$$CH_3COCH_3 \rightarrow CO + C_2H_6, \quad (23)$$

$$CH_3COCH_2CH_3 \rightarrow CO + \tfrac{1}{3}(C_2H_6 + C_3H_8 + C_4H_{10}), \quad (24)$$

$$CH_3COCH_2CH_2CH_2CH_3 \xrightarrow{15} CH_3COCH_3 + CH_3CH=CH_2. \quad (25)$$

These results indicate that the lower ketones undergo a primary decomposition into radicals which combine to give hydrocarbons whereas higher ketones decompose in the primary step according to the equation:



(26)

followed by isomerization on the wall or in the condensate, of the enolic form of the ketone to the ordinary form, CH_3COR. With more complicated higher ketones and aldehydes both processes occur[16] but this might be expected since there would be some shielding effect of the negative oxygen atom. We may note that the conclusion that aldehydes decompose mainly in one act according to the equation [17] $RCHO \rightarrow RH + CO$ is in disagreement with the conclusions of Section 7.

[14] Norrish, Crone and Saltmarsh, J. Chem. Soc. 145 (1934); Spence and Wild, ibid., 352 (1937) have shown that below 60°C, diacetyl is formed, so that presumably the primary step is formation of methyl and acetyl radicals.

[15] Norrish and Appleyard, J. Chem. Soc. 874 (1934).

[16] Bamford and Norrish, J. Chem. Soc. 1504 (1935).

[17] Norrish and Bamford, Nature **140**, 195 (1937); Norrish and Kirkbride, J. Chem. Soc. 1518 (1932); Norrish, Trans. Far. Soc. **30**, 107 (1934); idem., Acta Physica Chemica URSS, **3**, 171 (1935).

9. Experimental Objections

There are a number of experimental results,[18] such as the enlargement of rings by the use of diazomethane, that appear to contradict the views expressed in the preceding sections. Since this reaction and many others occur in solution and require a consideration of the effect of solvent, acid or basic catalysts, etc., we will omit from consideration all reactions that occur in condensed systems. However, there are two gaseous reactions that require some discussion because they appear to lead to the conclusion that shielded carbon atoms are subject to attack by radicals.

The effect of deuterium atoms on ethane has been recently studied [19] and the authors concluded that the main reaction could be represented by the equation,

$$D + C_2H_6 \rightarrow CH_3 + CH_3D.$$

This is an example of reaction (9) which we have rejected mainly on the ground of the shielding effect of the hydrogen atoms surrounding the carbon atoms. However, we have discussed this question with Professor Taylor and an interpretation of his experiments consistent with the scheme presented in our paper has proved to be possible; Professor Taylor will discuss this question in a future paper.

The second reaction occurs in the decomposition of the *n*-heptyl radical which appears to decompose in part to give a ring hydrocarbon, possibly cyclohexane.[20] Presumably the radical polymerization of olefins yields naphthenic hydrocarbons by a similar mechanism. A unimolecular decomposition of the heptyl radical into cyclohexane and a methyl radical would mean an attack by the open end of the radical on a shielded carbon atom. However, it is possible that an attack by another radical might remove a second hydrogen atom from an appropriate position and thus lead to ring closure. Also in this case both the reaction mechanism and the final products are not very well known and so definite conclusions cannot be reached at present.

[18] Mosettig and Burger, J. Am. Chem. Soc. **53**, 2295 (1931); Robinson and Smith, J. Chem. Soc. 371 (1937).

[19] Trenner, Morikawa and Taylor, J. Chem. Phys. **5**, 203 (1937). See also Chadwell and Titani, J. Am. Chem. Soc., **55**, 1363 (1933); Steacie, J. Chem. Phys., **6**, 37 (1938).

[20] Rice and Polly, Ind. Eng. Chem. **27**, 915 (1935).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Vapor-Liquid-Solution Displacements in Vibration Absorption Bands

To aid us in an interpretation of the structure of the absorption bands of water molecules in CS_2 and CCl_4 solutions and during other studies we have made observations on the displacements of certain relatively sharp infra-red absorption bands. A graphical summary of some of the data is given in Fig. 1. The $\Delta\nu$ wave number shifts are given with

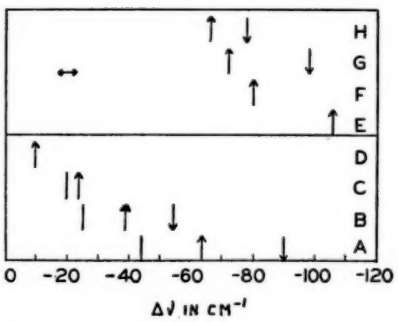


FIG. 1. Wave number displacements from vapor positions. *A-D*: CH bands. *E-H*: OH bands. *A*: chloroform, 1.145μ; *B*: chloroform, 1.680μ; *C*: ethyl alcohol, 1.730μ; *D*: formic acid, 1.727μ; *E*: formic acid, 1.435μ; *F*: ethyl alcohol, 1.395μ; *G*: water vapor (unresolved *Q* branch), 1.379μ; *H*: water vapor (unresolved *Q* branch), 1.875μ.

respect to the vapor positions. Upward arrows, downward arrows and simple lines indicate $C\epsilon l_4$ solution, CS_2 solution and pure liquid displacements, respectively. The concentrations of the solutions were not the same; the greatest concentration was 0.86 mole per liter in ethyl alcohol. The length of the double-headed horizontal arrow indicates the half-slit-width in wave numbers, 5 cm^{-1}, corresponding to 0.2 mm on the record plate. A shift of this amount can be observed easily by the superposition of two transparent records.

The figure reveals the following facts:

(1) A comparison of displacements in *A-D* with those in *E-H* indicates that in general band positions of the CH type are less dependent upon the surrounding medium than are those of the OH type.

(2) Comparisons of *A* with *B*, and of *G* with *H*, indicate a dependence of shift upon the magnitude of the frequency.

(3) The shifts are greater in the nonpolar solvents than in the pure liquids.

(4) In every instance CS_2 has a greater effect than CCl_4.

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July 13, 1938.

On the Question of the Intra- and Intermolecular "Hydrogen Bond" and the Absorption Spectra in the Near Infra-Red

A large number of publications have appeared particularly in this journal, on the information given by the absorption spectra in the near infra-red in regard to inter- and intramolecular bonds. Many authors do not seem to know of the researches we have pursued on this subject since 1932 in Professor Cotton's laboratory, Paris, with the help of several co-workers: Mrs. Marie Freymann, MM. P. Barchewitz, J. Guéron, A. Naherniac, B. Vodar, Yeou Ta and others. We think therefore that we should sum up the main results we obtained, with reference to the original publications.

In 1932[10] we have shown that the absorption spectra in the near infra-red permit the study of the phenomena of molecular associations: by heating (or diluting in CCl^4 for instance) an alcohol or an acid, we have shown that the intensity of the characteristic band of the OH nonassociated groups increases; this essential result has been mentioned several times since by many authors. Later researches, made by Errera and his co-workers,[5] by ourselves[15] . . . have extended our results and confirmed Barchewitz' suggestions.[2] In alcohols, for instance, there are at least two OH bands: the one, we have called $(OH)_v$, characteristic of the nonassociated OH groups, as in vapor; it is the sharp band we have studied, the intensity of which increases with the temperature. The other, called $(OH)_S$, characteristic of the associated OH groups, as in solid, a very broad band, the intensity of which decreases when the temperature increases.

The appearance of this latter band is connected with the phenomenon of so-called "hydrogen bonds" (3, 4, 6, 14, etc. . . .). In a note to the *Bulletin Société Chimique de France*[14] we have distinguished, as follows, the intra- and intermolecular bonds.

Intramolecular "hydrogen bond"

- Chelation[12, 18]
- Ketone-enol isomerism[12, 18]
- Amide tautomerism[12]

Intermolecular "hydrogen bond"

- Bond between the molecules of two different substances
  - oxonium compounds
    - with HOR (Aceton, dioxan, ···)[13, 15]
    - with HCl (aether, alcohol, ···)[16]
  - ammonium compounds
    - with HOR (Amines, nitrils, ···)[13]
    - with HCl[11]
- Bond between the molecules of the same substance (molecular association)
  - Alcohols, acids[10, 15]
  - Oximes[12']
  - Hydrogen chloride liquefied gas[17]

Let us emphasize a few points:

In the intramolecular bond (chelation, ketone-enol isomerism) the $(OH)_v$ band disappears as Wulf, Liddel and their co-workers have shown;[7] but $(OH)_s$ appears[18] reversing certain erroneous experimental results. Our work, with Mrs. Freymann, has shown that, contrary to the classical chemical formula of the tautomerism of amides, the $(OH)_v$ band does not appear and the (NH) band is weak.[12]

For the intermolecular bonds between different substances, the numerous examples we have given[13, 15] seem to be based upon experimental data more precise than the interesting researches made by Gordy at the same time. We add that the *hydrogen chloride solutions*

$$\frac{R}{R'}>O\cdots H\cdots Cl \qquad \text{and} \rightarrow N\cdots H\cdots Cl$$

(two examples we think we can compare) do not appear to have been studied so far. As to the "*phenomenon of dissimulation for the tetracoordinated nitrogen*," we refer to our general work[12] and to the thesis of Mrs. Freymann (in print). We mention only that, in a quite general way the (NH) band disappears or decreases in the aqueous solutions in which nitrogen is tetracoordinated. For instance $NH_4^+Cl^-$, $RNH_3^+Cl^-$, $NH_3^+CH_2COO^-$, $\left[Co\begin{matrix}(NH_3)_5\\H_2O\end{matrix}\right]Cl_3$, · · · (refer also to Edsall).[4']

For the intramolecular bonds between molecules of the same substance, our researches[10, 15] and Naherniac's studies[9] do not seem to have been noticed by Badger and Bauer[1] who, besides, have thoroughly confirmed our own results.

The example of the oximes $\frac{R}{R'}>C=N-OH$[12'] supplies another instance of molecular association that had not yet been observed. Finally, we have just shown with Mr. Vodar and Mr. Yeou Ta that liquefied HCl presents two vibration bands, one characteristic of the nonassociated molecules (second harmonic about 1.22μ), the other characteristic of the associated molecules (about 1.29μ); the latter decreases when the temperature increases from -80 to $+14°C$, which shows *the association of liquefied* HCl.[17]

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Paris, France,
July 1, 1938.

[1] R. Badger, S. Bauer, J. Chem. Phys. **4**, 711 (1936); **5**, 839 (1937).
[2] P. Barchewitz, Comptes rendus Acad. Sci. **203**, 1244 (1936).
[3] R. Barnes, L. Bonner and E. Condon, J. Chem. Phys. **4**, 772 (1936).
[4] A. Buswell, V. Deitz and W. Rodebush, J. Chem. Phys. **5**, 501 (1937).
[4'] J. Edsall, J. Chem. Phys. **4**, 1 (1936).
[5] J. Errera and P. Mollet, Comptes rendus Acad. Sci. **204**, 259 (1937).
[6] R. Gillette and A. Sherman, J. Am. Chem. Soc. 1135 (1936).
[7] Hilbert, Wulf, Hendricks, and Liddel, Nature **135**, 147 (1935).
[8] W. Gordy, Phys. Rev. **50**, 1151 (1936).
[9] A. Naherniac, Comptes rendus Acad. Sci. **138**, 1685 (1934); Ann. de physique **7**, 528 (1937).
[10] R. Freymann, Comptes rendus Acad. Sci. **195**, 39 (1932); Ann. de physique **20**, 243 (1933).
[11] J. Job, M. and R. Freymann, Comptes rendus Acad. Sci. **200**, 1043 (1935); M. Freymann and P. Rumpf, Comptes rendus Acad. Sci. **201**, 606 (1935); M. and R. Freymann and P. Rumpf, J. de phys. **7**, 30 (1936).
[12] M. and R. Freymann, Comptes rendus Acad. Sci. **202**, 1850 (1936); J. de phys. **7**, 476 and 506 (1936).
[12'] M. and R. Freymann, Comptes rendus Acad. Sci. **202**, 312 (1936).
[13] R. Freymann, Comptes rendus Acad. Sci. **204**, 41 (1937); M. Freymann, Comptes rendus Acad. Sci. **204**, 261 (1937).
[14] M. and R. Freymann, Bulletin Soc. Chim. Franc. **4**, 944 (1937).
[15] R. Freymann, Comptes rendus Acad. Sci. **204**, 1063 (1937); P. Barchewitz and R. Freymann, Comptes rendus Acad. Sci. **204**, 1729 (1937).
[16] R. Freymann and J Guéron, Comptes rendus Acad. Sci. **205**, 859 (1937).
[17] B. Vodar, R. Freymann and Yeou Ta, Bulletin Soc. Française Phys. n°415, p. 41 S (1938).
[18] R. Freymann, Comptes rendus Acad. Sci. **206**, 1812 (1938)